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CHEMICAL SCIENCES

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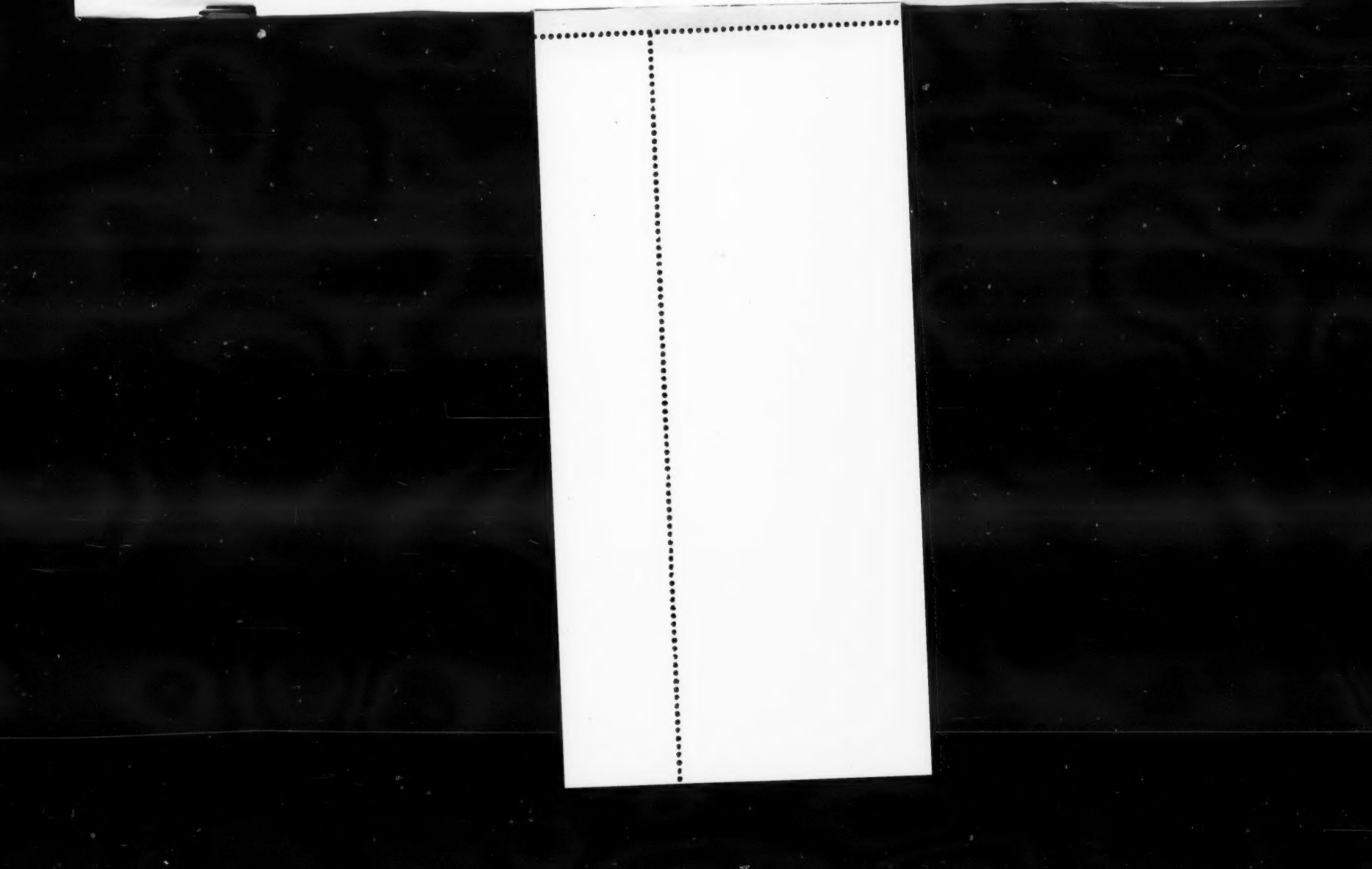
Please tear on the dotted line and attach the Erratum strip on page 791, Section B, Canadian Journal of Research, Volume 27, October 1949.

ERRATA

1. In Fig. 3, R_5 should not be shown connected to the junction of R_3 and R_4, but should be connected to the other end of R_3.

2. In the calculation of the reduced intensity for benzene using $\lambda = 4358$Å, the refractive index increment for polystyrene in benzene at $\lambda = 5461$Å was used in error. This increment is 5% higher for the blue line so that the corrected value of the reduced intensity for benzene is $R = 36.7 \times 10^{-6}$ cm.$^{-1}$ at 25°C. and $\lambda = 4358$Å.



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SYNTHESES DE LA *DL*-PROLINE A PARTIR DE L'α-PIPERIDONE[1]

PAR ROGER GAUDRY ET LOUIS BERLINGUET

Abstract

By treatment of α-piperidone with sulphuryl chloride, β,β'-dichloro-α-piperidone was obtained. It was hydrolyzed to α,α'-dichloro-δ-amino-*n*-valeric acid, which was simultaneously reduced and cyclized to DL-proline, by low pressure hydrogenation, using Raney nickel, in alkaline solution. All the intermediate compounds were identified and characterized. The over-all yield of DL-proline is 33% calculated from α-piperidone.

α-Piperidone was hydrolyzed to δ-amino-*n*-valeric acid, and the δ-phenylureido-*n*-valeric and δ-phthalimido-*n*-valeric acids were prepared. Halogenation of δ-phthalimido-*n*-valeric acid gave excellent yields of the α-bromo and α-chloro acids. These acids were hydrolyzed to the α-halogenated-δ-aminoacids. On treatment with alkali, they gave DL-proline in 56% and 50% yields respectively, from α-piperidone.

Halogenation of δ-phenylureido-*n*-valeric acid gave the dibromo and the dichloro acids, which ring-close immediately into derivatives of α-piperidone.

The different behavior of δ-benzoylamino, δ-phthalimido, and δ-phenylureido derivatives of *n*-valeric acid with halogens, or halogenating agents, is noted.

Introduction

La proline a été synthétisée pour la première fois par Willstätter en 1900 (14). Plusieurs autres synthèses ont été publiées depuis, mais aucune ne peut être considérée comme facile et satisfaisante. Ces méthodes peuvent se subdiviser en trois groupes principaux, à savoir:

1°— La condensation du chlorure de triméthylène avec un ester malonique ou ses dérivés.

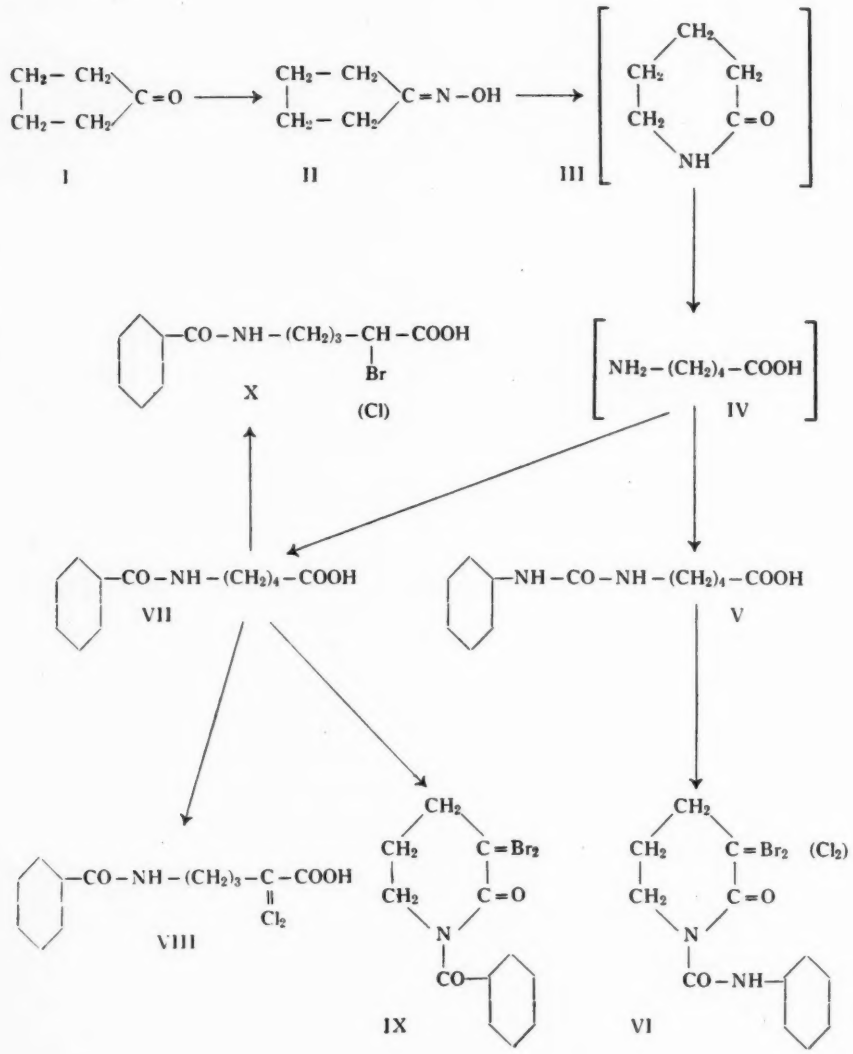
2°— La réduction catalytique de dérivés du pyrrole.

3°— L'ouverture de l'anneau des pipéridines ou de l'α-pipéridone substituées.

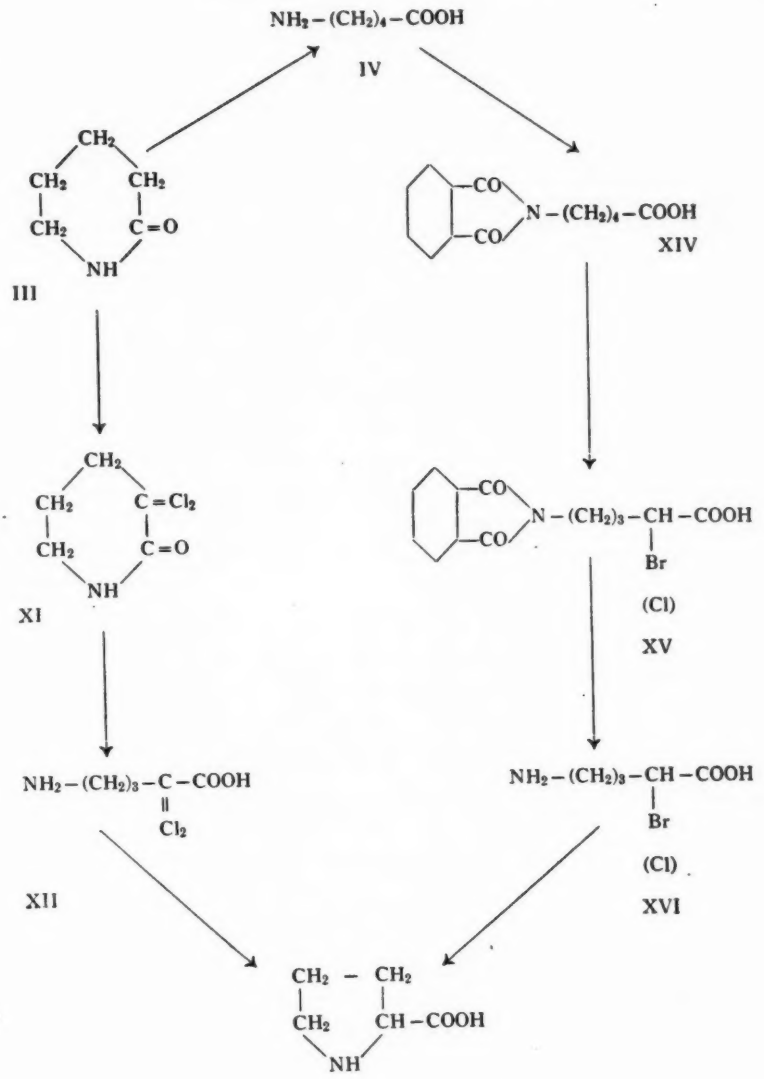
Puisque les condensations effectuées avec le bromure ou le chloro-bromure de triméthylène donnent souvent de faibles rendements, et que par ailleurs, les réductions de dérivés du pyrrole requièrent des hydrogénations à haute pression, il semble que les meilleures méthodes de synthèses soient celles qui utilisent les pipéridines ou les pipéridones substituées comme intermédiaires.

Parmi celles-ci, mentionnons la méthode classique de Fischer et Zemplen (7, 8), modifiée récemment par Maedo et Nozoe (12), et Dunn, Corse et Hillis (4). Ces auteurs, de même que Schniepp et Marvel (13), et Fox, Dunn et Stoddard (9), ont aussi utilisé cette méthode pour la synthèse de la DL-ornithine.

[1] *Manuscript reçu le 2 mars 1950.*
Contribution du Département de Biochimie, Faculté de Médecine, Université Laval, Québec, Qué.



Toutes ces synthèses utilisent l'acide δ-benzoylamino-*n*-valérianique (VII) obtenu soit à partir de l'oxyme de la cyclopentanone (II), soit par oxydation du dérivé benzoylé de la pipéridine. L'acide est bromé en position alpha, et le produit obtenu est hydrolysé et cyclisé en proline, ou aminé et hydrolysé en ornithine.



La méthode est simple, mais peu satisfaisante, parce que le dérivé bromé ne peut être obtenu que sous forme d'huile impure, et aussi parce que les rendements rapportés pour la bromuration de l'acide δ-benzoylamino-*n*-valérianique (VII) ne sont que d'environ 50%, à cause de la formation de N-benzoyl-β,β′-dibromo-α-pipéridone (IX) comme sous-produit.

Une autre synthèse de la proline à partir de l'α-pipéridone (III) par l'intermédiaire de la β,β′-dichloro-α-pipéridone (XI) a été décrite par Heymons (11). La pipéridone dichlorée est hydrolysée en acide α,α′-dichloro-δ-amino-*n*-valérianique (XII) qui est subséquemment réduit et cyclisé en proline (XIII) par l'amalgame de sodium.

Albertson et Fillman (2) ont récemment décrit une méthode beaucoup meilleure. Ils obtiennent la DL-proline par l'intermédiaire des composés suivants: l'ester 2-cyanoéthylmalonique, la β-carbéthoxy-α-pipéridone, la β-chloro-β′-carbéthoxy-α-pipéridone et l'acide α-chloro-δ-amino-*n*-valérianique. Cette synthèse exige cependant une hydrogénation à haute pression et le rendement total en proline n'est que de 20%.

Le but de notre travail était d'étudier les possibilités de synthèse de la DL-proline à partir de la pipéridone, d'abord en améliorant la synthèse originale de Heymons, puis en modifiant la méthode de Fischer en remplaçant le radical benzoylé de l'acide δ-amino-*n*-valérianique aussi obtenu de l'α-pipéridone, par le radical phénylcarbamylé et le radical phtalylé.

Nous avons préparé l'α-pipéridone (III) avec un rendement de 60% à partir de l'oxyme de la cyclopentanone (II) en utilisant la méthode décrite par Eck et Marvel (5). L'α-pipéridone en présence de chlorure de sulfuryle donne à froid un produit cristallin que nous avons isolé et identifié comme étant le chlorhydrate de l'α-pipéridone. A des températures plus élevées, il y a substitution complète des deux atomes d'hydrogène par le chlore, et nous avons isolé la β,β′-dichloro-α-pipéridone (XI) avec un rendement de 70%. Tous nos essais pour préparer la β-chloro-α-pipéridone ont échoué. Par hydrolyse acide de la β,β′-dichloro-α-pipéridone nous avons obtenu l'acide α,α′-dichloro-δ-amino-*n*-valérianique (XII) avec un rendement de 80%. Cet acide n'avait pas été caractérisé auparavant, et nous l'avons identifié en le transformant en dérivé benzoylé (VIII), qui contrairement au dérivé dibromé correspondant ne se cyclise pas spontanément en N-benzoyl, β,β′-dichloro-α-pipéridone (IX). Nous avons effectué la réduction et la cyclisation simultanées de l'acide α,α′-dichloro-δ-amino-*n*-valérianique (XII) en proline, par hydrogénation catalytique à basse pression, en présence d'alcali et de nickel Raney. Nous avons isolé la DL-proline sous forme de sel de cuivre avec un rendement de 55% calculé à partir de l'acide α,α′-dichloro-δ-amino-*n*-valérianique. Puisqu'Albertson et Fillman (2) ont obtenu un rendement de 66% en chlorhydrate de proline, par cyclisation de l'acide α-chloro-δ-amino-*n*-valérianique, il semble que le rendement de la réduction elle-même soit excellent.

Nous avons donc amélioré la méthode de Heymons en substituant le chlorure de sulfuryle au pentachlorure de phosphore, ce qui nous a permis d'isoler sous forme cristalline la pipéridone dichlorée ainsi que l'acide α,α′-dichloro-δ-amino-*n*-valérianique (XII). Nous avons aussi remplacé la réaction avec l'amalgame de sodium incommode par une hydrogénation et une cyclisation effectuées à basse pression et à température de la chambre. Nous avons aussi augmenté le rendement de la cyclisation de 47% à 55%.

Au cours de leur synthèse de l'ornithine et de la proline, Fox, Dunn et Stoddard (9) n'isolent pas l'α-pipéridone, mais l'hydrolysent aussitôt en acide δ-amino-*n*-valérianique (IV) qu'ils précipitent sous forme de dérivé benzoylé (VII) avec 70% de rendement, en ajoutant du chlorure de benzoyle à la solution alcaline de l'acide aminé. Cette technique augmente le rendement, parce qu'il y a toujours entre 10% et 15% de pipéridone qui est hydrolysée pendant le réarrangement de l'oxyme de la cyclopentanone, ce qui constitue une perte si la pipéridone seule peut être utilisée.

Pour conserver l'avantage de cette méthode, mais aussi pour éviter les difficultés de l'halogénation de l'acide δ-benzoylamino-*n*-valérianique, nous avons préparé l'acide δ-phényluréido-*n*-valérianique (V) avec un rendement de 76%, en ajoutant l'isocyanate de phényle au produit du réarrangement et d'hydrolyse de l'oxyme de la cyclopentanone. Malheureusement, l'halogénation de l'acide δ-phényluréido-*n*-valérianique (V) nous a donné quantitativement les dérivés dihalogénés qui se cyclisent aussitôt en dérivés de la pipéridone (VI). Nous avons établi la structure de la N-phénylcarbamyl-β,β'-dichloro-α-pipéridone (VI) en la comparant avec le produit obtenu par traitements successifs de l'α-pipéridone par l'isocyanate de phényle et par le chlorure de sulfuryle. Le dérivé ainsi obtenu est identique à celui qu'on prépare par traitement de l'acide δ-phényluréido-*n*-valérianique (V) avec le chlorure de sulfuryle.

Nous avons alors préparé le dérivé phtalylé (XIV) avec un rendement de 86%, en chauffant l'anhydride phtalique avec l'acide δ-amino-*n*-valérianique (IV) obtenu par hydrolyse acide de l'α-pipéridone pure (III). Nous avons constaté que le brome et le chlorure de sulfuryle donnent respectivement l'acide α-bromo-δ-phtalimido-*n*-valérianique et l'acide α-chloro-δ-phtalimido-*n*-valérianique (XV) avec d'excellents rendements, sans aucune trace des produits dihalogénés. L'hydrolyse acide de ces acides, suivie de leurs cyclisations, nous a donné la DL-proline, avec des rendements comparables à ceux d'Albertson et de Fillman (2) pour la même cyclisation. Il nous est alors possible d'isoler la proline par la méthode d'Albertson et de Fillman (2) qui évite l'emploi des sels de cuivre et d'argent. Le rendement total en DL-proline à partir de l'α-pipéridone (III) est de 56% par l'intermédiaire du dérivé bromé et de 50% par l'intermédiaire du dérivé chloré.

Notons que l'acide α-bromo-δ-phtalimido-*n*-valérianique (XV) avait déjà été préparé par E. Fischer (6) par condensation de la phtalimide de potasse avec le bromure de triméthylène et l'ester malonique, suivie de bromuration, d'hydrolyse et de décarboxylation. Par amination de cet acide α-bromo-δ-phtalimido-*n*-valérianique (XV), Fischer avait obtenu un rendement de 42% en ornithine, isolée sous forme d'acide ornithurique. La nouvelle synthèse de la proline que nous venons de décrire pourrait donc devenir intéressante pour la synthèse de l'ornithine.

A la suite de ces résultats, il est remarquable de constater que lorsqu'un radical phtalimidé occupe la position delta de l'acide *n*-valérianique (XIV),

l'halogénation donne exclusivement les acides mono-halogénés, alors que la présence d'un radical phényluréidé (V) favorise la formation des acides dihalogénés, qui se cyclisent aussitôt en dérivés de la pipéridone; mais la présence d'un radical benzamidé en position delta de l'acide *n*-valérianique (VII) permet l'obtention d'un mélange des acides mono et dihalogénés. Puisque ces trois substituants sont respectivement acide, basique et neutre, il est plus facile de comprendre les comportements différents de ces acides *n*-valérianiques substitués.

Les chromatogrammes sur papier que nous avons obtenus à divers stages des synthèses de la proline, confirment également les résultats expérimentaux d'Albertson et de Fillman, à savoir que l'hydrolyse acide seule d'un acide α-halogéné-δ-amino-*n*-valérianique (XVI) ne donne pas de proline et que la cyclisation n'a lieu qu'en milieu alcalin.

Partie expérimentale

Chlorhydrate de l'α-pipéridone

Dans un ballon refroidi à l'extérieur par un bain de glace on place 9.9 g. (0.1 mole) d'α-pipéridone (III) en solution dans 50 ml. de tétrachlorure de carbone. Tout en maintenant une agitation vigoureuse, on fait tomber goutte à goutte 13.5 g. (0.1 mole) de chlorure de sulfuryle. Aussitôt apparaît un solide blanc, insoluble dans le tétrachlorure, qui après avoir été filtré et séché pèse 10.0 g., 75%. On obtient un rendement presque quantitatif en concentrant le filtrat. Ce produit est recristallisé dans un minimum d'alcool absolu. Les cristaux obtenus ont un point de fusion s'échelonnant de 120° à 170° C.* et se décomposent avec émission de HCl. Ce chlorhydrate est très hygroscopique; très soluble dans l'eau, il donne un précipité de chlorure d'argent avec le nitrate d'argent. Calculé pour $C_5H_{10}ONCl$: N, 10.40% Cl, 26.2%. Trouvé: N, 10.50% Cl, 25.6%.

β,β'-dichloro-α-pipéridone (XI)

On place dans un bain de glace, un ballon contenant 4.6 g. d'α-pipéridone (III) et 0.7 g. de phosphore rouge et on ajoute, goutte à goutte avec agitation, 50 ml. de chlorure de sulfuryle. Lorsque tout le chlorure de sulfuryle a été introduit, le ballon est chauffé pendant une heure dans un bain-marie maintenu à 80° C. On évapore à sec sous pression réduite et on obtient un résidu gommeux, auquel on ajoute de l'eau glacée par petites portions. Il se produit une vive réaction, et un produit blanc précipite et se solidifie entièrement au froid. P.f. 163°–164° C. Litt.: 107° C. (?) (11). Rendement: 5.2 g., 66.6%. Calculé pour $C_5H_7OCl_2N$: N, 8.34% Cl, 42.2%. Trouvé: N, 8.40% Cl, 41.2%.

Acide α,α'-dichloro-δ-aminovalérianique (XII)

Dans un ballon muni d'un réfrigérant on place 2.0 g. d'α-pipéridone dichlorée (XI) et 100 ml. de HCl concentré. Le mélange est ensuite chauffé à reflux

**Les points de fusion ne sont pas corrigés.*

pendant 17 h. On évapore à sec, et le chlorhydrate de l'acide aminé est dissous dans l'eau et porté à l'ébullition avec du noir animal pendant quelques minutes, pour décolorer la solution. Après avoir filtré, on évapore à sec à nouveau et on reprend le résidu par l'alcool absolu. Par addition de la quantité théorique de pyridine, soit 1 ml., l'acide dichloré précipite à froid, sous forme d'un solide blanc cristallin. On le recristallise d'un mélange d'eau et d'alcool. P.f. 199° C. avec décomposition et dégagement de gaz. Rendement: 1.79 g., 80.5%. Le rendement à partir de l'α-pipéridone, sans isoler la pipéridone dichlorée est d'environ 60%. Calculé pour $C_5H_9O_2NCl_2$: N, 7.73% Cl, 38.2%. Trouvé: N, 7.70% Cl, 37.4%.

Acide α,α'-dichloro-δ-benzoylamino-n-valérianique (VIII)

On ajoute à une solution alcaline 1.86 g. (0.01 mole) d'acide α,α'-dichloro-δ-amino-*n*-valérianique (XII) et 1.15 g. (0.01 mole) de chlorure de benzoyle. Après avoir agité pendant quelques minutes, on acidifie avec de l'acide chlorhydrique et par refroidissement, l'acide α,α'-dichloro-δ-benzoylamino-*n*-valérianique (VIII) précipite. On le recristallise d'un mélange d'eau et d'alcool. P.f. 149° à 151° C. Rendement: 2.26 g., 78%. Calculé pour $C_{12}H_{13}O_3NCl_2$: N, 4.83% Cl, 24.5%. Trouvé: N, 4.76% Cl, 25.1%.

N-phénylcarbamyl-α-pipéridone

On place dans un petit ballon muni d'un tube réfrigérant, 1.4 g. (0.014 mole) d'α-pipéridone (III), 1.6 g. (0.014 mole) d'isocyanate de phényle et une trace de triéthylamine. On chauffe le mélange sur un bain-marie bouillant pendant trois heures. Après avoir refroidi le ballon sous un jet d'eau froide, on ajoute de l'eau au mélange, ce qui a pour effet de faire solidifier la masse. On filtre et on recristallise d'un mélange d'eau et d'alcool en parties égales. P.f. 96°–97° C. Rendement: 2.73 g., 94.0%. Calculé pour $C_{12}H_{14}O_2N_2$: N, 12.8%. Trouvé: N, 12.82%.

DL-proline (XIII)

On prépare le nickel Raney W-7 de la façon décrite par Adkins et Billica (1). L'appareil utilisé pour la réduction est un appareil à hydrogénation à basse pression (Parr).

On place dans le récipient un mélange de 1.8 g. d'acide α,α'-dichloro-δ-amino-*n*-valérianique (XII), 15.0 g. d'hydroxyde de sodium et 5.0 g. de nickel Raney W-7, dans 150 ml. d'eau. On introduit l'hydrogène jusqu'à ce que la pression atteigne 30 livres au pouce carré et on agite mécaniquement le récipient pendant cinq heures. A ce moment l'adsorption d'hydrogène est terminée.

Le nickel Raney est alors filtré, et on ajoute un excès d'acide chlorhydrique. La solution est évaporée sous pression réduite et on chauffe le résidu de chlorhydrate de proline et de chlorure de sodium dans l'alcool absolu. On filtre le chlorure de sodium insoluble et le filtrat est évaporé à sec. A ce stage, la

chromatographie sur papier n'indique que la présence de proline. Le chlorhydrate de proline est dissous dans l'eau et traité par l'hydroxyde d'argent, tel que décrit antérieurement (10). On isole la DL-proline sous forme de sel de cuivre bleu, qu'on recristallise d'une quantité minimum d'eau. Les cristaux bleus prennent, lorsque secs, une coloration violette très caractéristique du prolinate de cuivre. Rendement: 0.77 g., 55.0%. Calculé pour $C_{10}H_{16}O_4N_2Cu$: N, 9.62%. Trouvé: N, 9.53%.

Acide δ-phényluréido-n-valérianique (V)

On fait le réarrangement de deux portions de 10.0 g. d'oxyme de la cyclopentanone (II) de la façon décrite par Eck et Marvel (5), et on fait bouillir à reflux la solution acide pendant trois heures avec du noir animal. Après avoir filtré, on neutralise la solution limpide de l'acide δ-amino-*n*-valérianique (IV), et on ajoute un excès de 8.0 g. d'hydroxyde de sodium. Tout en maintenant une agitation efficace, on laisse tomber 23.8 g. (0.20 mole) d'isocyanate de phényle pendant une période de 30 min., et on continue l'agitation pendant une heure supplémentaire. On filtre la solution et tout en agitant, on acidifie par un excès d'acide chlorhydrique. L'acide δ-phényluréidé (V) précipite sous forme d'un solide blanc très lourd qu'on filtre aussitôt et qu'on recristallise d'un mélange à parties égales d'eau et d'alcool. L'acide δ-phényluréido-*n*-valérianique (V) est un solide blanc, qui cristallise en paillettes. Rendement: 36.8 g., 76.2%. P.f. 162° C. Calculé pour $C_{12}H_{16}O_3N_2$: N, 11.86%. Trouvé: N, 11.84%.

N-phénylcarbamyl-β,β'-dibromo-α-pipéridone (VI)

On place dans un ballon muni d'un réfrigérant, un mélange de 11.8 g. (0.05 mole) d'acide δ-phényluréido-*n*-valérianique (V), 1.0 g. de phosphore rouge et 40 ml. de tétrachlorure de carbone. On ajoute alors avec précaution, 10.0 ml. de brome. Il se produit aussitôt un vif dégagement de HBr. Le ballon est chauffé sur un bain-marie pendant trois heures, et l'excès de brome et de tétrachlorure est chassé par distillation sous pression réduite. Après avoir refroidi le résidu sous l'eau froide, on ajoute une solution saturée de bicarbonate de sodium et on laisse au repos pendant 10 h. On obtient un solide jaune insoluble, qui après filtration et séchage, pèse 17.0 g. (90.0%). Par recristallisation de l'alcool, on obtient un produit cristallin blanc. La N-phénylcarbamyl-β,β'-dibromo-α-pipéridone (VI) fond à 103°–104° C. Calculé pour $C_{12}H_{12}O_2N_2Br_2$: N, 7.45% Br, 42.5%. Trouvé: N, 7.56% Br, 43.3%.

N-phénylcarbamyl-β,β'-dichloro-α-pipéridone (VI)

A un mélange de 11.8 g. (0.05 mole) d'acide δ-phényluréido-*n*-valérianique, de 1.0 g. de phosphore rouge et de 40 ml. de tétrachlorure de carbone, placé dans un ballon muni d'un réfrigérant, on ajoute par portions, 50 ml. de chlorure de sulfuryle. Il se produit alors une vive réaction et l'acide δ-phényluréido-*n*-valérianique passe en solution. On chauffe le ballon au bain-marie pendant deux heures, et on chasse l'excès de chlorure de sulfuryle par distillation.

Après avoir ajouté une solution de bicarbonate de sodium, on laisse au repos pendant 10 h., après quoi, il ne reste plus qu'un solide jaune, qui filtré lavé et séché, pèse 13.5 g. (94.0%). La N-phénylcarbamyl-β,β'-dichloro-α-pipéridone (VI) se recristallise de l'alcool absolu. P.f. 109° C. Calculé pour $C_{12}H_{12}O_2N_2Cl_2$: N, 9.76%. Trouvé: N, 9.73%.

N-phénylcarbamyl-β,β'-dichloro-α-pipéridone (VI)

On ajoute 25 ml. de chlorure de sulfuryle à un ballon contenant 1.0 g. de N-phénylcarbamyl-α-pipéridone et on chauffe le mélange à reflux sur un bain-marie pendant deux heures. On évapore l'excès de chlorure de sulfuryle sous pression réduite. Le résidu est dissous dans l'alcool chaud et par addition de petites quantités d'eau, il se produit un léger trouble. On refroidit alors le mélange sous l'eau froide et il se forme un précipité blanc qu'on recristallise de l'alcool absolu. La N-phénylcarbamyl-β,β'-dichloro-α-pipéridone (VI) fond à 109° C. et n'abaisse pas le point de fusion d'un échantillon préparé par chloruration de l'acide δ-phényluréido-*n*-valérianique. Rendement: 0.9 g., 69.0%. Calculé pour $C_{12}H_{12}O_2N_2Cl_2$: N, 9.76%. Trouvé: N, 9.62%.

Acide δ-phtalimido-n-valérianique (XIV)

On chauffe à reflux dans un ballon, muni d'un réfrigérant, 19.8 g. (0.2 mole) d'α-pipéridone (III), 40 ml. d'eau distillée et 160 ml. d'acide chlorhydrique concentré. Après cinq heures d'ébullition, la solution est évaporée à sec et on obtient ainsi le chlorhydrate de l'acide δ-amino-*n*-valérianique.

Ce chlorhydrate est dissous dans un peu d'eau distillée et neutralisé à pH de 7.0 par une solution d'hydroxyde de sodium. On évapore à sec sous pression réduite, et on fait sécher le résidu, qui est un mélange de chlorure de sodium et d'acide δ-amino-*n*-valérianique (IV). Le poids de ce résidu est de 35.5 g.

On broie intimement dans un mortier 29.62 g. (0.20 mole) d'anhydride phtalique et le résidu obtenu. Le mélange est placé dans une grande éprouvette qui plonge dans un bain maintenu à une température de 185°–190° C. On agite le mélange au moyen d'une spatule de verre. Après quelques secondes, tout devient liquide et on observe un dégagement abondant d'eau, qui se condense sur les parois. La réaction est terminée au bout de 15 min. On refroidit l'éprouvette et le solide obtenu est recristallisé d'un mélange de 120 ml. d'alcool et de 680 ml. d'eau distillée. L'acide δ-phtalimido-*n*-valérianique (XIV) précipite rapidement en magnifiques cristaux, qui filtrés et séchés pèsent 42.2 g., 85.8%. P.f. 117°–118° C. Litt.: 117° C. (3). Calculé pour $C_{13}H_{13}O_4N$: N, 5.66%. Trouvé: N, 5.67%.

Acide α-chloro-δ-phtalimido-n-valérianique (XV)

On pulvérise intimement dans un mortier, 12.35 g. (0.05 mole) d'acide δ-phtalimido-*n*-valérianique et 1.0 g. de phosphore rouge. Ce mélange est placé dans un ballon muni d'un réfrigérant et par addition de 50 ml. de chlorure de sulfuryle il se produit un vif dégagement de gaz, en même temps que tout

passe en solution. On chauffe le ballon sur un bain-marie pendant trois heures, puis le chlorure de sulfuryle qui n'a pas réagit est distillé. Après avoir refroidi le ballon, on ajoute de petites portions de glace au résidu, ce qui a pour effet de faire cristalliser l'huile. Après un séjour de 24 h. au froid, on filtre le solide, on le pulvérise dans un mortier avec un peu d'eau distillée et on le sèche. Ce produit est l'acide α-chloro-δ-phtalimido-*n*-valérianique (XV) presque pur. Rendement: 13.88 g. (98.6%). P.f. 109° à 112° C. Calculé pour $C_{13}H_{12}O_4NCl$: N, 4.98% Cl, 12.6%. Trouvé: N, 4.90% Cl, 13.0%.

Chlorhydrate de l'acide α-chloro-δ-amino-n-valérianique (XVI)

On fait bouillir à reflux pendant 11 h., une solution contenant 10.5 g. (0.037 mole) d'acide α-chloro-δ-phtalimido-*n*-valérianique (XV) et 200 ml. d'acide chlorhydrique concentré. On ajoute alors 200 ml. d'eau et on porte le tout au froid. L'acide phtalique précipite et on le recueille par filtration. Le filtrat est extrait deux fois à l'éther, ce qui a pour effet d'enlever les dernières traces d'acide phtalique, et l'éther est chassé par distillation sous pression réduite. Le résidu huileux obtenu est le chlorhydrate de l'acide α-chloro-δ-amino-*n*-valérianique (XVI). A ce stage, la chromatographie sur papier n'indique aucune trace de DL-proline.

Acide α-bromo-δ-phtalimido-n-valérianique (XV)

On triture dans un mortier 12.35 g. (0.05 mole) d'acide δ-phtalimido-*n*-valérianique (XIV) et 1.0 g. de phosphore rouge. Ce mélange est ensuite placé dans un ballon muni d'un réfrigérant et contenant déjà 40 ml. de tétrachlorure de carbone. On ajoute alors goutte à goutte 10 ml. (0.20 mole) de brome et on note aussitôt un vif dégagement de HBr. Après quatre heures d'ébullition, on évapore sous pression réduite, le tétrachlorure de carbone et le brome qui n'a pas réagi. Au résidu refroidi, on ajoute environ 150 g. de glace pulvérisée, et on laisse le ballon au froid pendant 24 h. L'huile obtenue cristallise alors en un solide blanc, qu'on filtre, qu'on pulvérise dans un mortier avec de l'eau et qu'on sèche. L'acide α-bromo-δ-phtalimido-*n*-valérianique presque pur, est recristallisé du benzène. Rendement: 15.97 g., 97.1%. P.f. 123° à 125° C. Litt.: 127°–128° C. (3). Calculé pour $C_{13}H_{12}O_4NBr$: N, 4.29% Br, 24.5%. Trouvé: N, 4.27% Br, 24.0%.

Chlorhydrate de l'acide α-bromo-δ-amino-n-valérianique (XVI)

On fait bouillir à reflux pendant 16 h. une solution contenant 16.3 g. (0.05 mole) d'acide α-bromo-δ-phtalimido-*n*-valérianique (XV) et 250 ml. d'acide chlorhydrique. On obtient le chlorhydrate de l'acide α-bromo-δ-amino-*n*-valérianique (XV) de la même façon que celle décrite pour le chlorhydrate de l'acide α-chloro-δ-amino-*n*-valérianique. Le chlorhydrate est sous forme de résidu huileux, qui semble difficile à recristalliser d'un mélange d'éther et d'alcool (2). L'analyse par chromatographie sur papier ne permet pas déceler de DL-proline.

DL-proline (XIII)

On ajoute 20.0 g. d'hydroxyde de sodium à une solution contenant le chlorhydrate de l'acide α-bromo-δ-amino-*n*-valérianique (XVI) préparé de la façon décrite plus haut, et on laisse reposer le tout pendant quatre jours à température de la chambre. Après avoir ajouté un excès d'acide chlorhydrique concentré, on évapore à sec, sous pression réduite. Le chlorhydrate de proline obtenu ainsi est dissous dans l'alcool chaud et on filtre le chlorure de sodium. On évapore à nouveau le filtrat sous pression réduite. Le résidu est dissous dans l'eau et traité de la façon décrite antérieurement (10). Une fois les dernières traces d'acide chlorhydrique enlevées, on fait bouillir la solution contenant la DL-proline avec un excès de carbonate de cuivre pendant une heure. On filtre l'excès de carbonate de cuivre et on concentre le filtrat. Par refroidissement, les cristaux bleus de prolinate de cuivre précipitent. On les recueille par filtration et on les sèche pour enlever l'eau de cristallisation. On obtient ainsi des cristaux violets de prolinate de cuivre. Rendement: 4.85 g., 67.0%. Calculé pour $C_{10}H_{16}O_4N_2Cu$: N, 9.62%. Trouvé: N, 9.58%.

La méthode décrite plus haut a aussi été utilisée pour la cyclisation de l'acide α-chloro-δ-amino-*n*-valérianique et nous avons obtenu un rendement de 3.17 g. de prolinate de cuivre, à partir de 10.46 g. d'acide α-chloro-δ-phtalimido-*n*-valérianique, soit un rendement de 58.5%.

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CONTRIBUTION TO THE SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS[1]

I. DEUTEROPOLYMETHYLENE

By Leonard C. Leitch, Paul E. Gagnon, and Adrien Cambron

Abstract

An improved method of preparing polymethylene, $(CH_2)_n$, by the decomposition of diazomethane is described. A new polymer, polyethylidene, $(CH_3.CH)_n$, has been obtained from diazoethane by the same reaction. Diazomethane-d_2 is reported for the first time. A new deuterated polymer, $(CD_2)_n$, obtained by the decomposition of diazomethane-d_2 has been synthesized.

Introduction

The deuteron-induced reaction, $D(d,n)He^3$, is known to give good yields of monochromatic neutrons (8). The development of suitable targets containing deuterium would facilitate further investigation of this nuclear reaction. For this purpose, a substance was needed which had the following properties: (*a*) a high content of deuterium atoms; (*b*) thermal stability to ion bombardment; and (*c*) a low vapor pressure.

The synthesis of such compounds was disclosed in a Norwegian patent (12) which described the preparation of deuterated hydrocarbons by the Fischer–Tropsch process. By passing a mixture of deuterium and carbon monoxide in the ratio 2:1 over a cobalt catalyst at 180° to 220°C., a small quantity of paraffin wax was formed in addition to liquid hydrocarbons. However, the yield of wax, m.p. 65° C., was only 2.6 gm. per cu. m. of deuterium. According to Fischer and Pichler (3) the optimum conditions for wax formation with a cobalt catalyst containing a small percentage of thorium are attained at 175° C. under 15 atm. pressure. Even then, a fair amount of liquid hydrocarbons and oils was formed so that the yield of wax was 60 gm. per cu. m. of synthesis gas. A few years later, Fischer and Bufflieb (4) reported the formation of paraffin wax melting as high as 134° C. in good yields when using a ruthenium catalyst and operating at 100 atm. or more.

Dr. W. E. Hanford of the Kellogg Corporation, New York, who was consulted, suggested that instead of the Fischer–Tropsch method, the polymerization of ethylene-d_4 or the decomposition of deuterodiazomethane be tried for the preparation of deuteropolymers.

The first alternative appeared satisfactory in most respects except that the polymerization of ethylene requires very high pressures and closely controlled

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conditions. Regarding the second, a methylene polymer was first observed many years ago by Bamberger and Tschirner (1) as a by-product in the reaction between diazomethane and phenylhydroxylamines. They also obtained it by allowing a solution of diazomethane to stand over pieces of unglazed porcelain. The yield in both instances was very low. The product was a white amorphous substance: m.p. 126° to 127° C. The analytical figures corresponded to the formula $(CH_2)_n$; for this reason Bamberger called the substance "polymethylen." The same product was also obtained by Meerwein, Rathjen and Weiner (9) in addition to other compounds by exposing a solution of diazomethane to sunlight. In their case, the yield was also very low, in fact lower than 3%; 2.7 gm. was formed from 350 gm. of diazomethane.

A sample of polymethylene was first prepared with unglazed porcelain according to Bamberger and Tschirner's method. Our results confirmed theirs. It was then decided to try to improve the yield by using a suitable catalyst. The catalytic action of finely divided copper in the decomposition of diazo compounds is well known. For example, the preparation of indolyl ethyl acetate by the action of diazoacetic ester on indole in the presence of copper powder was described by Jackson and Manske (7). Nesmejanow (11) was likewise able to replace the diazonium group in aromatic compounds by mercury, using copper powder. It therefore seemed very likely that freshly precipitated copper might improve the yield of polymer.

This was very successfully realized when an ether solution of diazomethane was added to a suspension in ether of finely divided copper. Evolution of nitrogen began at once and after a day the solution was colorless. On digesting the residue left after decanting the ether with nitric acid, a white flocculent precipitate, m.p. 126° to 127° C., remained behind which was identical with the polymer reported in earlier work. The yields in different experiments varied between 30 and 40%.

A similar reaction took place when diazoethane in ether was added to copper powder. Since the polyethylidene was soluble in ether, only a trace was deposited on the catalyst. The polymer was recovered in this case by removal of the solvent and treatment of the residue with ethanol to induce it to crystallize. Polyethylidene, $(CH_3.CH)_n$, was obtained in 33% yield: m.p. 96° to 97°C.

The next objective was to repeat this work using diazomethane-d_2 in order to obtain the deuterated polymer, $(CD_2)_n$. The diazomethane-d_2 required was prepared in two ways. The first method involved the preparation of nitromethane-d_3 which was obtained by exchanging ordinary nitromethane with deuterium oxide as described by Wilson (13). The nitro compound was then reduced to the amine with deuterium. With aqueous potassium cyanate, the amine gave methyl-d_3-urea, which, when treated with nitrous acid, gave nitrosomethyl-d_3-urea. Diazomethane-d_2 was obtained when the nitroso compound was added to a mixture of ether and sodium deuteroxide. When nitrosomethyl-d_3-urea was added to ordinary aqueous alkali, the diazome-

thane-d_2 initially formed exchanged its deuterium with the hydrogen present and gave ordinary diazomethane.

This observation indicated that deuterodiazomethane could easily be prepared directly from diazomethane. In fact, by shaking ordinary diazomethane with deuterium oxide, a product rich in deuterium resulted. By repeating the operation twice more with fresh portions of heavy water, a sample of diazomethane-d_2 nearly free from hydrogen was obtained. In these exchange experiments there is always some loss due to the formation of methyl-*d* alcohol-*d*, CH_2DOD. In fact, this observation was made by Halford, Anderson, and Kissin (6) and also by Beersman and Jungers (2). No mention was made in either paper of exchange having taken place.

The diazomethane-d_2 thus prepared was decomposed in the presence of copper as was the protium compound. The yields were similar. The properties of deuteropolymethylene, $(CD_2)_n$, resemble those of polymethylene. In addition, it may be noted that this polymer has a deuterium content even greater than that of deuterium oxide.

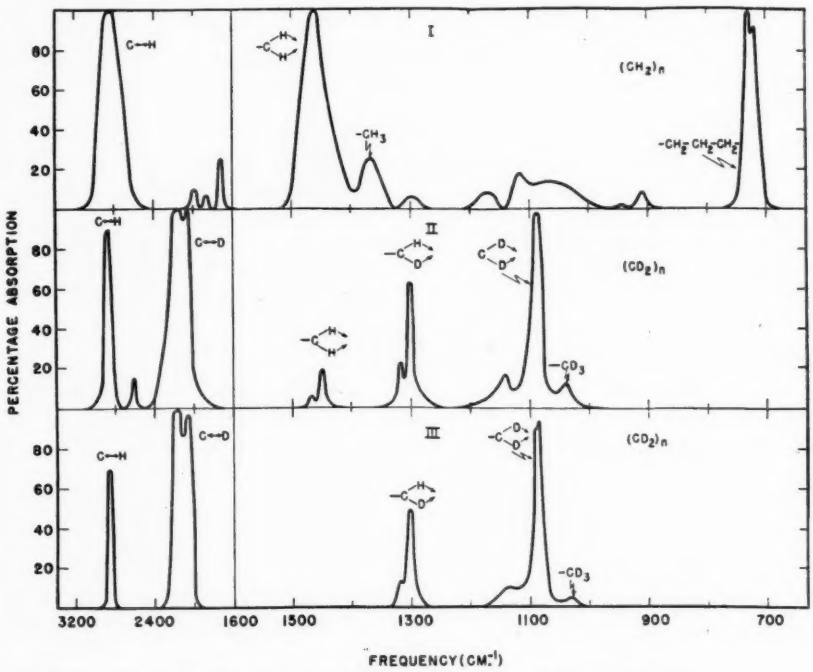
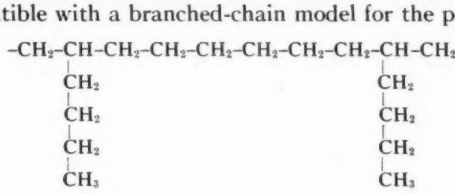


FIG. 1. *Infrared absorption spectra of polymethylene and deuteropolymethylene.*

The infrared absorption spectrum of polymethylene and deuteropolymethylene (Fig. 1) was examined by Dr. D. A. Ramsay who interpreted the bands as follows:

"In the spectrum of the light polymer (I of Fig. 1), the 2900 cm.$^{-1}$ absorption may be attributed to stretching vibrations of the C–H bonds present and is observed in the spectra of all aliphatic hydrocarbons. The 1460 cm.$^{-1}$ absorption is due to symmetrical deformation vibrations of the CH_2 groups present, while the absorption at 1375 cm.$^{-1}$ indicates the presence of methyl groups. A strong absorption in the region of 725 cm.$^{-1}$ is characteristic of long chain paraffins containing three or more adjacent CH_2 groups. The position of this band varies from 740 to 720 cm.$^{-1}$ with increasing length of the CH_2 chain, hence the presence of two bands in the spectrum of the polymer at 720 cm.$^{-1}$ and 731 cm.$^{-1}$ suggests the presence of CH_2 chains differing in chain length. This is compatible with a branched-chain model for the polymer.



It may be noted that each of the side-chains terminates in a methyl group, thus the intensity of the 1375 cm.$^{-1}$ band may be used to determine the number of methyl groups present and hence the degree of branching of the polymer.

In the spectrum of the deuterated polymer (II of Fig. 1), the principal absorption occurs in the region of 2200 and 1100 cm.$^{-1}$ and may be attributed to stretching vibrations of the C–D bonds and deformation vibrations of the CD_2 groups present. A weak absorption band also occurs at 1040 cm.$^{-1}$ and may be assigned to CD_3 groups. It may be noted that these frequencies are roughly $\sqrt{2}$ times lower than the corresponding frequencies in the light polymer. The absorptions at 2900 cm.$^{-1}$ and 1460 cm.$^{-1}$ in the spectrum of the heavy polymer indicate the presence of residual CH and CH_2 groups, while the absorption band at 1300 cm.$^{-1}$ corresponds to the CHD deformation vibration observed in the spectra of the partially deuterated methanes. Thus, while the deuterated polymer consists mainly of CD_2 groups, the infrared spectrum also indicated the presence of CHD and CH_2 groups.

The spectrum of the polymer (III of Fig. 1) obtained by decomposing diazomethane-d_2 which had been prepared from nitrosomethyl-d_3-urea closely resembles that of the polymer which resulted from the decomposition of diazomethane-d_2 prepared by exchange."

Experimental

Polymethylene, $(CH_2)_n$

Zinc dust (6.0 gm.) was added to a stirred solution of copper sulphate pentahydrate (25.0 gm.) in water (250 ml.) placed into a round-bottomed flask (0.5 liter). After stirring for an hour, the precipitated copper was allowed to settle and the supernatant liquid was decanted. The residue was washed

twice with distilled water (200 ml.), then with methanol and finally with ether. A titrated solution of diazomethane in ether was prepared from methylnitrosourea (30.0 gm.) and slowly added over a period of two hours to a suspension of the precipitated copper in a little ether. Evolution of nitrogen began at once; after one day, the ether solution was colorless. It was decanted from the copper and discarded. The residue was digested on the steam bath for a few hours with 40 ml. of nitric acid (25%). The white, flocculent, amorphous precipitate was collected on a Büchner funnel, washed several times with hot water, then with 50% ethanol–water. Occasionally, the precipitate retained a faint bluish color. The color was removed by suspending the powder in a little dilute nitric acid for a few minutes and filtering once more. The addition of a trace of capillary active material was helpful. The yield calculated from the diazomethane was 0.7 to 0.8 gm. (30 to 40%). The product melted at 127° to 128° C. and could not be recrystallized. Although it dissolves in high-boiling solvents such as cumene, butanol or tetrachlorethane, it separates as a gelatinous mass on cooling. Evaporation of the solvent leaves a residue resembling paraffin wax. Towards acids and bases, the substance also behaves like paraffin. It is practically unaffected by hot concentrated hydrochloric or nitric acids or by alkali. Hot concentrated sulphuric acid causes charring. When heated alone in a test tube, it chars somewhat, leaving a waxy deposit on the cold end of the tube. It is self-plasticizing and can be molded.

Several other catalysts were tried. An alloy of copper and silver was very active at first, judging from the vigorous evolution of nitrogen which took place, but was ineffective as soon as the surface of the catalyst became covered with a layer of polymer. Naturkupfer C was quite active but gave a greyish polymer which could not be purified. Raney nickel gave a very inferior yield of polymer. Freshly precipitated silver prepared in the same manner as the copper was completely inert. Calc. for $(CH_2)_n$: C, 85.71; H, 14.29%. Found: C, 86.02; H, 13.68%.

Polyethylidene, $(CH_3.CH)_n$

Diazoethane was prepared in 50% yields by adding, as rapidly as possible, ethylnitrosourea (30.0 gm.) to a stirred mixture of ether (300 ml.) and a solution of potassium hydroxide (50%, 90 ml.) kept at −15° C. in an acetone-dry ice bath. When the reaction was carried out at 0° C. or at higher temperature, the yield was never more than 25% of the theoretical amount. The diazoethane in the ether was titrated in the usual manner.

A solution of diazoethane (7.0 to 8.0 gm.) in ether was added dropwise to a suspension of copper (6.0 gm.) precipitated with zinc as described in the preparation of polymethylene. A tall spiral condenser was used to prevent loss of diazoethane with nitrogen. When the ether became colorless, it was decanted from the copper and saved. The copper residue left only traces of polymer when dissolved in nitric acid (25%). The ether solutions from three

experiments, corresponding to 24.0 gm. of diazoethane, were combined and fractionated in a 60 cm. Stedman column. The thick syrupy residue that remained after evaporating all the ether was heated under reduced pressure in a water bath at 50° C. This treatment caused the mass to swell and crystallize. The solid was triturated with 25 ml. of ethanol, in which it is insoluble, and filtered. The yield of this material was 4.0 gm. (33%), m.p. 94 to 96° C. Calc. for $(CH_3.CH)_n$: C, 85.71%; H, 14.29%. Found: C, 85.77%; H, 14.17%.

Nitromethane-d_3, $CD_3.NO_2$

Nitromethane-d_3 was prepared from nitromethane and a solution of sodium deuteroxide (0.02 *M* NaOD) in deuterium oxide by a method similar to that used by Wilson (13). The nitromethane was first dried over phosphorus pentoxide and fractionated in a Stedman column, 300 mm. in height and 25 mm. diameter, equipped with a stillhead of the total-condensation partial take-off type. The fraction, boiling at 100.5–100.8° C., d_0^{25}: 1.1180 was used.

A mixture of nitromethane (25 ml.) and 0.02 *M* NaOD in deuterium oxide (25 ml.) was heated for 24 hr. at 110° C. in a sealed tube placed in a rocker type of shaker. After cooling, the tube was opened and its contents was transferred to a small separatory funnel. The lower layer containing the deuterated nitromethane was drawn off, dried over phosphorus pentoxide, and distilled under reduced pressure. Yield: 22.0 gm., d_0^{25}: 1.1672. The upper layer containing deuterium oxide was shaken with a small quantity of absolute ether, which was separated and used for extraction in later experiments. The deuterium oxide itself was recovered by distillation under reduced pressure. Its density was 1.0600, instead of 1.0970, the density of the starting material.

The deuterated nitromethane obtained was treated again with a solution of 0.02 *M* NaOD in deuterium oxide and the products of the reaction were separated and purified as before. The density of the nitromethane had risen to 1.1785. After a third exchange, a product was obtained which was practically free from hydrogen, as shown by an infrared absorption spectrum determination. The over-all yield was 17.0 gm. (59%) of nitromethane-d_3, d_0^{25}: 1.1832.

Methyl-d_3-amine Hydrochloride, $CD_3.NH_2$, HCl

A palladium catalyst suspended on carbon was prepared according to the directions of Mozingo (10). Deuterium chloride was generated from benzoyl chloride and deuterium oxide and absorbed in a known weight of deuterium oxide (5). A mixture of nitromethane-d_3 (6.0 gm.) and deuterium oxide which contained sufficient deuterium chloride to neutralize the methylamine formed was treated with deuterium under 3 atm. pressure in the presence of 0.4 gm. catalyst. The reduced solution was filtered under pressure by forcing it to pass through a porous glass disk and was evaporated to dryness *in vacuo*. The deuterium oxide recovered was used with the same catalyst. The yield of methyl-

amine-d_5 hydrochloride-*d* was 5.9 gm. (90%). The product was recrystallized from hot *n*-butanol: m.p. 227° to 228° C. The butanol contained appreciable amounts of butanol-*d*, on account of the exchange reaction: $CD_3.ND_2.DCl + 3C_4H_9OH \rightleftharpoons CD_3.NH_2.HCl + 3C_4H_9OD$ and was saved for future use.

Methyl-d_3-nitrosourea, $CD_3.N(NO).CO.NH_2$

Methylamine-d_3 hydrochloride (23.0 gm.) was dissolved in water (130 ml.), potassium cyanate (18.4 gm.) was added, and the solution was boiled gently for 15 min. The methyl-d_3 urea obtained was then added slowly to a stirred solution of sulphuric acid (23 gm.) in water (150 ml.) kept at 0° C. The solid product that separated was filtered off, washed with a little ice-water, and dried in a desiccator. The yield of methyl-d_3-nitrosourea was 23.0 gm. (60%).

Diazomethane-d_2

(*a*) *From Nitrosomethyl-d_3-urea*

A concentrated solution of sodium deuteroxide was prepared by adding clean sodium (5.0 gm.; 0.46 mole) in small portions to deuterium oxide (30.0 ml.; 99.7 mole % D) in a 100 ml. round-bottomed flask fitted with a mechanical stirrer and reflux condenser. The mixture was cooled in a bath of acetone – dry ice at about 0°C. When the sodium had completely dissolved, absolute ether (100 ml.) was added and then nitrosomethyl-d_3 urea (5.3 gm.; 0.05 mole) in small portions. The ice-cold solution of diazomethane-d_2 in ether was separated in a funnel and used in the preparation of deuteropolymethylene as described below.

(*b*) *From Diazomethane and Deuterium Oxide by Exchange*

A solution of diazomethane in ether was prepared by the usual method from methylnitrosourea and dried over pellets of sodium hydroxide. It was then stirred for two hours with a solution of potassium hydroxide (17 gm.) in deuterium oxide (25 ml.), of a 5% solution of sodium deuteroxide, prepared by dissolving 1 gm. of sodium in small pieces in 25 ml. of deuterium oxide. Alternatively, a 2% solution of potassium carbonate was also used as an exchange medium. After repeating the experiment twice with fresh portions of deuterium oxide, diazomethane-d_2 nearly free from hydrogen could be obtained but there was considerable loss of diazomethane owing to decomposition.

Deuteropolymethylene, $(CD_2)_n$

Diazomethane-d_2 (3.0 gm.), prepared by either of the methods previously mentioned, was added to an equal weight of copper powder as catalyst. The deuteropolymethylene was isolated as described in the case of the protium compound. The yield was 0.53 gm. (53%): m.p. 122° to 123° C. Calc. for $(CD_2)_n$: C, 75.00%. Found: C, 77.38%.

The analytical figures indicate the presence of residual hydrogen in the compound. This was confirmed by comparing its infrared spectrum with that of polymethylene (Fig. 1).

Acknowledgments

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THE CHEMISTRY OF ETHYLENE OXIDE

I. AN ANALYSIS FOR ETHYLENE OXIDE[1]

By A. M. Eastham and G. A. Latremouille

Abstract

Accurate and convenient analyses for ethylene oxide can be obtained using 1% periodic acid in dilute perchloric acid as reagent. The time required is less than an hour and the precision is about 0.1–0.2%.

Ethylene oxide is usually determined by absorbing the oxide in dilute hydrochloric acid solutions saturated with calcium or magnesium chloride, and back-titrating the excess acid with standard alkali. This method, developed by Lubatti (9, 10) from earlier work by Dechert (4, 5, 6), is rapid and fairly accurate but is rather inconvenient to handle; it is unsatisfactory for aqueous solutions of oxide, and is quite dependent upon a satisfactory grade of calcium or magnesium chloride (8).

Branham and Shepherd (1) have developed a gasometric method in which the ethylene oxide, mixed with air as a carrier, is absorbed in 50% sulphuric acid. A reproducibility of 0.05% is claimed for ethylene oxide – carbon dioxide mixtures but the method is obviously limited in its applications.

Swern *et al.* (11) describe a general method for the estimation of oxirane compounds in which the oxide ring is allowed to react with hydrogen chloride in anhydrous ether, and excess acid then determined by titration. This method appears to be highly accurate but is limited to water- or alcohol-free samples.

In the present work an effort has been made to develop an analysis of greater accuracy and more general application than those mentioned above, by taking advantage of the quantatitive oxidation of glycol by periodic acid. If the hydrolysis of ethylene oxide to glycol could be accomplished equally quantatitively, this method should be very precise.

Experimental

Ethylene Oxide

Two samples of oxide were used, one a regular commercial material, and the other a sample supplied by the Matheson Company, stated to have a purity of at least 99.5 mole %. Both samples gave identical analyses throughout and in neither case was the analysis improved by distillation through a 40 plate Stedman column at high reflux ratios, or by passing the oxide in the gas phase over soda lime. Mass spectrometer examination indicated the two samples to be essentially identical and to contain no more than traces of impurities other

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than carbon dioxide and acetaldehyde. These latter two materials could not be estimated since they are isomeric with ethylene oxide, but must be essentially absent since the distillation and soda lime treatments did not alter the analyses.

Accurate samples of ethylene oxide were obtained by drawing the liquid oxide into small (1 cc.) weighed bulbs, having capillary tips. The tips were quickly sealed in a flame and the bulbs reweighed.

Analytical Procedures

The reagent to be tested was placed in a 500 cc. wide-mouthed bottle having a ground glass stopper, and a bulb of ethylene oxide was added. A glass rod was placed between the bulb and stopper in such a way that forcing down the stopper simultaneously closed the bottle and broke the bulb.

(*a*) Lubatti's reagent was prepared from reagent grades of magnesium and calcium chloride and from a technical grade of magnesium chloride. In general, best results were obtained by titrating to a pH value determined by preliminary runs, but satisfactory end points were usually obtained with methyl orange indicator when pure reagents were used.

(*b*) Dry hydrogen chloride, dissolved in dioxane and in absolute ethanol, was examined as a reagent for comparison with the results of Swern *et al.* When using dioxane – hydrogen chloride mixtures, a small amount of water was added to the flask through a dropping funnel before opening for titration, in order to minimize the evaporation losses of hydrogen chloride. Phenolphthalein was a satisfactory indicator for back-titration with standard sodium hydroxide. Reaction of the oxide and hydrogen chloride was usually complete within 10 min.

(*c*) 1% Periodic acid solutions were prepared by dissolving about 12 gm. paraperiodic acid in one liter of water. To 100 cc. of this solution was added a 0.1–0.2 gm. sample of ethylene oxide and the mixture allowed to stand for five or six hours. The excess periodic acid was then determined by the method of Fleury (7) or by that of Voris *et al.* (12), and a blank, containing 25 cc. of the periodic acid solution, analyzed under the same conditions. Since one mole of periodic acid is equivalent to one mole of ethylene oxide, the oxide can be calculated from these two titrations.

For determining periodate, the method of Fleury is preferred to that of Voris *et al.*, since the latter requires very close control of the pH during titration.

The analytical procedure was checked occasionally by substituting standardization grade arsenious oxide for ethylene oxide. A carefully weighed sample of arsenious oxide was dissolved in sodium hydroxide by the usual methods, neutralized to methyl orange and added to the periodic acid in the presence of sodium bicarbonate. The excess periodic acid was then determined as before. Results were accurate to $\pm$ 0.1%.

(*d*) To determine whether increasing the acidity would decrease reaction time, 1% periodic acid solutions were prepared in dilute sulphuric and perchloric acid solutions. The precision of these reagents was tested exactly as before, but the reaction times were determined by titrating aliquots of a reaction mixture at intervals until the titer reached a constant value. This value was assumed to correspond to 99.6% ethylene oxide in the sample.

The results of all these experiments are summarized in Tables I and II.

TABLE I

Reagent	No. of analyses	% Oxide found (average)	Maximum deviation from the average
1. Lubatti			
(*a*) 0.1 *N* HCl + c.p. $MgCl_2$	4	97.7	± 0.5%
(*b*) + c.p. $CaCl_2$	11	97.4	± 0.8%
(*c*) + tech. $MgCl_2$	5	94.0	± 0.4%
2. 0.4 *N* HCl in abs. ethanol	6	90.7	± 0.2%
3. 0.5 *N* HCl in abs. dioxane	17	99.4	± 0.5%
4. 0.04 *N* H_2SO_4 followed after 3 hours by 1% HIO_4	5	96.3	± 0.2%
5. 1% HIO_4 in water	13	99.7	± 0.2%
6. 1% HIO_4 in 0.02 *N* H_2SO_4	4	98.9	± 0.2%
7. 0.12 *N* $HClO_4$	2	99.7	± 0.2%
8. 0.15 *N* $HClO_4$	5	99.5	± 0.2%
9. 0.26 *N* $HClO_4$	2	99.6	± 0.1%

TABLE II

Reagent	% Recovery of ethylene oxide				
	15	30	45	60	75 min.
1% HIO_4 in 0.10 *N* $HClO_4$	76.4	92.8	96.6	99.6	99.6
0.20 *N* $HClO_4$	93.0	98.5	99.3	99.6	99.6
0.40 *N* $HClO_4$	88.2	99.6	99.6		

Discussion

The results of these experiments show clearly that accurate analyses for ethylene oxide can be obtained using as reagents either hydrogen chloride in an inert medium, or periodic acid in aqueous solution. The results appear to be distinctly more accurate than those obtained with Lubatti's reagents and the periodic acid method is very convenient to handle.

In 1% aqueous periodic acid the analysis requires about five hours, owing largely to the slow rate of hydrolysis. However, since this rate is dependent upon the hydrogen ion concentration (2), it should be possible to speed up the analysis by adding an acid which does not react with ethylene oxide or periodate. Sulphuric acid is unsuitable, owing presumably to the formation of

diethylene glycol, perhaps through an intermediate hydroxyethyl-sulphate. Perchloric acid, however, is satisfactory and as is seen in Table II, markedly decreases the reaction time.

No effort has been made to work at temperatures above 25°C.

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THE ESSENTIAL OIL OF *PICEA MARIANA* (MILL.) B.S.P.[1]

By A. C. Shaw

Abstract

The essential oil of *Picea mariana* has been prepared and its major constituents separated by fractional distillation. Evidence for the presence of 15 constituents has been obtained, and santene, tricyclene, *l*-α-pinene, *l*-camphene, *l*-β-pinene, myrcene, *d*-Δ^3-carene, *dl*-limonene, terpinolene, *dl*-camphor, *l*-borneol, and *l*-bornyl acetate have been identified with certainty.

Introduction

Picea mariana(Mill.), or black spruce, is widely distributed throughout North America, from the Yukon territories south to Alabama, and from the maritime provinces to the Pacific coast. Since it is frequently confused with other species of spruce and hemlock during distillation, its essential oil is a constituent of many of the "spruce" and "hemlock oils" of commerce. The oil has not previously been examined in detail, although the distillation of a species designated only as "*Picea mariana*" in a yield of 0.57%; D_{19} 0.9274 has been reported (9).

Experimental

Preparation of the Essential Oil

The foliage and terminal branches of *Picea mariana*, collected in June 1948, were distilled with steam at 90 lb. pressure for eight hours. The oil, obtained in a yield of 0.461%, had the following properties: d_{20}^{20} 0.9085; n_D^{20} 1.4696; α_D^{30} −32.1°; saponification number, 119.7; saponification number after acetylation, 123.3; aldehyde content as citral, 0.3%; ketone content as carvone, 1.0%; acid value, 0.44.

Fractional Distillation of the Oil

A preliminary distillation under reduced pressure, through a 15 in., unjacketed column, consisting of eight pear-shaped bulbs, gave the fractions listed in Table I.

TABLE I

Fraction	Boiling range, °C.	n_D^{20}	d_4^{20}	% by weight
A	43–70° (10 mm.)	1.4683–1.4768	0.848–0.870	48.0
B	70–100° (10 mm.)	1.4768–1.4648	0.870–0.980	37.5
C	80–110° (1 mm.)	1.4648–1.5031	0.980–0.915	6.5
Residue and loss				8.0
				100.0

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One liter of Fraction *A* was carefully fractionated, using a 6 ft., 25 mm. I.D. Podbielniak Hyper-Cal column at a reflux rate of 300–400 ml. per hr. Distillate was collected in 25 ml. volumes. The properties of the fractions are listed in Table II.

TABLE II

Fraction*	B.p., ° C.	n_D^{20}	d_4^{20}	α_D	Fraction*	B.p., ° C.	n_D^{20}	d_4^{20}	α_D
1	58 (48 mm.)	1.4669	0.865	0.00	20	71 (48 mm.)	1.4705	..	..
2	65	1.4671	0.867	− 0.33	21	71	Solid at R.T.		
3	67	1.4634	0.871	− 9.17	22	71	15 g. solid		
4	69	1.4649	0.863	−21.61	23	71-73	55 g. solid		
5	69.5	1.4655	0.863	−22.94	24	74-78	17 g. solid		
6	69.5	1.4658	0.862	−26.36					
7	70	1.4660	0.863	−34.23	25	165.8 (757 mm.)	1.4785	0.870	−21.08
8	70	1.4669	0.863	−42.15	26	166.1	1.4789	0.872	−18.49
9	71	1.4674	0.863	−44.77	27	166.7	1.4741	0.830	− 7.02
10	71	1.4677	0.864	−47.79	28	168.1	1.4712	0.811	+ 2.92
11	71	1.4682	0.864	−51.82	29	170.1	1.4713	0.828	+ 6.63
12	70.5	1.4685	0.864	−55.63	30	170.9	1.4716	0.846	+ 9.20
13	70.5	1.4690	0.864	−57.14	31	171.5	1.4720	0.853	+ 9.52
14	70.5	1.4691	0.865	−59.22	32	171.9	1.4724	0.857	+ 8.90
15	70.5	1.4696	0.865	−63.29	33	173.0	1.4720	0.864	+ 5.10
16	70.5	1.4697	0.865	−65.02	34	176.9	1.4735	0.860	−15.95
17	71	1.4697	0.865	−65.88	35	178.5	1.4758	0.846	−27.85
18	71	1.4701	0.866	−66.69	36	178.5	1.4752	0.844	−30.15
19	71	1.4702	0.866	−67.58	37	178.5	1.4745	0.848	−30.35

**Fractions 1 to 24 inclusive were distilled at 48 mm. pressure, and reflux ratio 15/1. Fractions 25 to 37 inclusive were distilled at 20 mm. pressure, and reflux ratio 20/1.*

Fractions 21–24 were maintained in a molten condition during distillation by means of a infrared lamp.

Boiling points of Fractions 25 to 37 were determined at atmospheric pressure on small samples of distillate.

Distillation of 1250 ml. of Fraction *B* at reflux ratio 30/1 gave the fractions listed in Table III.

TABLE III

Fraction	Volume, ml.	n_D^{20}	d_4^{20}	α_D	B.p., ° C.	% Alcohols*	% Ketones†
38	10.0	1.4753	0.878	−18.9	183.0	....	....
39	"	1.4820	0.883	−17.7	186.3	10.0	5.1
40	"	1.4856	0.876	−11.5	187.8	....	....
41	"	1.4875	0.874	− 7.6	188.3	....	4.5
42	"	1.4800	0.872	− 4.0	188.8	9.3	....
43	"	1.4973	0.876	− 1.7	190.1	12.5	10.3
44	"	1.4806	0.911	+ 1.1	196.4	43.0	45.2
45	23.3	1.4714	0.934	+ 6.5	203.4	54.6	42.6
46	10.0	1.4780	0.962	+19.9	209.0	61.0	....
47	10.0	1.4774	0.965	+25.6	209.4	....	10.3
48	20.0	1.4750	0.960	+22.3	211.1	70.5	8.6
49	3.3	1.4771	0.959	+ 6.2	212.0	....	....

**By acetylation.*
†By reaction with hydroxylamine hydrochloride.

Solid *l*-borneol crystallized from Fraction 49 and plugged the side arm of the column. By reducing the reflux ratio to 10/1 the distillation of borneol in a less pure, liquid state was possible. After removal of 50 ml. of a borneol-rich fraction in this way, the remainder of the oil distilled with almost constant properties in excellent agreement with those of *l*-bornyl acetate: n_D^{20} 1.4640 to 1.4645; d_4^{20} 0.987; α_D −35.5° to −36.5°; m.p. 22.4° to 23.4° C.

On repeated fractional distillation through the unpacked column employed in the preliminary distillation, 750 ml. of Fraction *C* yielded 300 gm. of bornyl acetate, and the three fractions described in Table IV.

TABLE IV

Fraction	B.p., ° C. (1 mm.)	n_D^{20}	d_4^{20}	α_D^{25}	Ester No.	Ester No. after acetylation	Acid No.	Wt., gm.
I	80–90	1.505	0.904	+38°	0	11	0.0	100
II	90–110	1.495			43	126	0.8	40
III	110–130	1.510			38	191	0.8	30

Since the material boiling above 110° C. (1 mm.) underwent extensive decomposition to nonvolatile tars during distillation, refractionation could not be continued to the point where relatively homogeneous products were obtained.

Identification of Constituents

Santene

Fraction 1, when treated with nitrous acid according to Müller (10) gave santene nitrosite in 49% yield. It formed blue platelets from methanol, melting at 124–125° C. alone, or in admixture with an authentic sample prepared from oil of *Abies siberica*. Aschan (1) records m.p. 124–125° C.

Tricyclene

The high density of Fraction 3 was remarkable. Redistillation gave about 3 gm. of a waxy white volatile solid with an odor reminiscent of camphene, but which was optically inactive, and stable to permanganate. After purification, by treatment with excess aqueous 2% permanganate at room temperature, followed by crystallization from methanol and sublimation from sodium, it melted at 61–64° C. and boiled at 153° C.

A synthetic sample was prepared by the method of Aschan (2). Chlorination of 50 gm. of α-pinene produced 6 gm. of β-camphor dichloride m.p. 173–174° C., which, when refluxed in 20% ether solution for 24 hr. with 3 gm. of sodium gave tricyclene m.p. 60–65° C., in an all over yield of 3.2%.

Both natural and synthetic hydrocarbons were obtained as waxy solids with no apparent crystal structure. Their melting points were rather indistinct but were not depressed on mixing. The absorption spectra of both compounds were determined between 3–4 μ and 7–13 μ in a 0.025 mm. cell in carbon disulphide solution, with a Perkin–Elmer spectrometer. The region 4–7 μ was obscured by carbon disulphide absorption. Perfect coincidence of absorption maxima was observed throughout the region examined and variations in optical density were within the experimental error. The absorption spectrum of tricyclene is shown in Fig. 1.

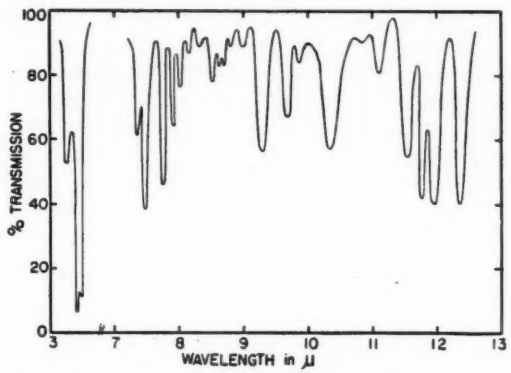

FIG. 1. *Absorption spectrum of tricyclene in 46% (by weight) solution in carbon disulphide.*

l-α-Pinene

Fractions 6 and 7 (34 gm.) when oxidized with neutral permanganate by the method of Delepine (6), gave 22 gm. of crude acids, separated by fractional crystallization from benzene–hexane mixtures into a more soluble and a less soluble fraction. From the latter was obtained 5.6 gm. of *dl*-pinonic acid, which after four crystallizations melted at 103-104° C., $[\alpha]_D$ −1.4° (c = 6.77 in chloroform). The more soluble fraction yielded 1.5 gm. of *l*-pinonic acid, m.p. 68–69.5° C, $[\alpha]_D$ −89.6° (c = 2.66 in chloroform), after crystallization from ethyl ether and then from water. The literature records m.p. 103–104° C. for the racemic (8), and m.p. 67–69° C., $[\alpha]_D^{25}$ −90° 33′ for active pinonic acid (3).

l-Camphene

Fraction 23 after crystallization from methanol followed by sublimation gave *l*-camphene melting at 47–48° C., $[\alpha]_D$ −97.5° (c = 10.56 in benzene). Hydration of 6 gm. of this material according to Bertram and Walbaum (4), gave an almost quantitative yield of isoborneol, melting at 210.5–212° C. after crystallization from hexane.

l-β-Pinene

Fractions 25 and 26 (10 gm.) were oxidized under essentially the same conditions as used for α-pinene. After concentration and cooling, the aqueous

oxidization liquors deposited 1.2 gm. of potassium nopinate. By acidification and chloroform extraction of the mother liquors, 3.5 gm. of acids was obtained, which, on treatment with 5% aqueous sodium hydroxide, deposited a sparingly soluble sodium salt, purified by crystallization from water. By acidification of the salt, and crystallization of the free acid from a mixture of benzene and hexane, nopinic acid was obtained, melting at 126–127° C. alone or in admixture with an authentic specimen.

Myrcene

A fraction, with properties n_D^{20} 1.4710, d_4^{20} 0.800, α_D + 0.83, b.p. 167° C. (757 mm.), was obtained by refractionation of Fractions 28 and 29. The maleic anhydride adduct, prepared and purified as described by Diels and Alder (7), crystallized from hexane in white platelets melting at 34–35° C. The yield was 68% of theoretical. The adduct was dissolved in warm 30% aqueous potassium hydroxide, and the solution acidified and extracted with ether. The viscous oil obtained on removal of the ether deposited granular crystals from acetonitrile, m.p. 118–120° C., raised to 120–122° C. by repeated crystallization. Diels and Alder record m.p. 34–35° C. for the adduct derived from myrcene, and m.p. 122–123° C. for the free acid.

d-Δ^3-Carene

Refractionation of Fractions 30 and 31 gave a liquid with properties n_D^{20} 1.4729; d_4^{20} 0.866; b.p. 172° C. (762 mm.), in excellent agreement with those reported by Simmonsen (12) for Δ^3-carene. The nitrosate, prepared in the usual way in a yield of 12%, melted with decomposition at 147° C., undepressed by an authentic specimen prepared from turpentine oil of *Pinus longifolia* Roxb.

dl- and l-Limonene

To a well cooled solution of 10 gm. of Fraction 36 in 10 ml. of isoamyl alcohol and 20 ml. of absolute ether, bromine was added dropwise until a persistent coloration was obtained. After evaporation of most of the ether, dipentene tetrabromide separated in 27% yield. After crystallization from ethyl acetate it melted at 124–125° C. alone or in admixture with an authentic sample. While the optically active tetrabromide was not isolated, the presence of about 24% of *l*-limonene would account for the observed rotation of −30°.

Terpinolene

Fraction 42 was distilled from sodium and brominated as above. After crystallization from ethanol 1.2 gm. of tetrabromide melting at 116–118° C. was obtained. Calc. for $C_{10}H_{16}Br$: Br, 70.1%. Found: 69.8%.

The melting point of the compound in mixture with dipentene tetrabromide was depressed about 20°, but in mixture with the tetrabromide of terpinolene was undepressed.

l-Borneol

The solid from Fraction 49, after crystallizing from hexane, melted at 204–205° C., $[\alpha]_D$ −31.5° (c = 9.83 in toluene). The *p*-nitrobenzoyl ester, prepared in almost quantitative yield from 0.6 gm. of material by boiling for five minutes with 0.75 gm. of the acyl chloride in pyridine, formed light yellow platelets from ethanol, melting at 136–137° C. after one crystallization.

l-Bornyl Acetate

Two samples, one collected early, and the other towards the end of the distillation of this fraction, were made to crystallize at dry ice temperatures. Their melting points, measured with an immersed thermometer were 22.4° and 23.4° C. respectively. Pickard and Kenyon (11) reported m.p. 27.4° C. for *l*-bornyl acetate with $[\alpha]_D$ −44°. Other properties of the fraction are in close agreement with those recorded by these investigators.

A solution of 20 gm. of ester and 12 gm. potassium hydroxide in 60 ml. of ethanol was boiled under reflux for 15 min., and then poured into 300 ml. of water. The *l*-borneol which separated (12.5 gm. after one crystallization) melted at 207.5–208° C., $[\alpha]_D$ −31.83° (c = 10.62 in toluene); *p*-nitrobenzoate m.p. 136–137° C. alone, or in admixture with the ester described in the preceding section. The aqueous liquors were extracted with ether, treated with carbon dioxide to remove free alkali, and evaporated to dryness. The residue was extracted with 50 ml. of boiling ethanol. After removal of the alcohol, the residue, weighing 7.5 gm., was boiled for one hour with 10 ml. of thionyl chloride, diluted with benzene, and filtered. The filtrate was cautiously treated with 11 gm. of aniline in 20 ml. of benzene, and the benzene solution washed with dilute acid, dilute base, and finally with water. The mass remaining after evaporation of the benzene was leached with boiling water. This extract, after decolorization with charcoal and cooling, separated 0.5 gm. of acetanilide melting at 113–115° C.

Camphor

Fraction 45 (10 gm.) in 150 ml. of ethanol was allowed to stand at room temperature for three weeks in the presence of 5 gm. of semicarbazide hydrochloride and 5 gm. of sodium acetate. After distillation of the solvent and removal of the unchanged terpenes in a current of steam, the residue, weighing 2.1 gm. after crystallization from ethanol, was leached with boiling acetonitrile. The insoluble fraction yielded 0.9 gm. of a semicarbazone melting at 234–235° C. Steam distillation of this material from 10 gm. of oxalic acid in 10 ml. of water regenerated a ketone melting at 171–174° C., $[\alpha]_D$ + 6° (c = 1.07 in ethanol), the X-ray diffraction pattern which was indistinguishable from that of camphor. The 2,4-dinitrophenyl hydrazone, prepared by refluxing the compound for 30 min., with 2,4-dinitrophenylhydrazine in ethanol containing 5% of sulphuric acid, formed orange needles from ethanol, melting at 164–166° C. alone, or in admixture with a known sample of *dl*-camphor

2,4-dinitrophenyl hydrazone. Table V lists the interplanar spacings* corresponding to the four most intense lines, for camphor and its 2,4-dinitrophenyl hydrazone.

TABLE V

X-RAY DIFFRACTION POWDER DATA

Copper K_α radiation. Intensities, visual estimation.

Camphor		*dl*-Camphor 2,4-dinitrophenyl hydrazone	
d (Å)	I (arbitrary units)	*d*	I
5.44	10	3.27	10
6.18	7	4.15	10
5.81	5	5.23	10
4.23	2	10.89	9

The more soluble semicarbazone melted at 188–192° C., but could not be obtained pure. It possibly contains *d*-camphor semicarbazone. The quantities obtained were not sufficient to permit regeneration of the ketone.

Terpene Alcohol

When heated at 100° C. for ½ hr. with α-naphthyl isocyanate, Fraction 47 yielded only a few milligrams of *sym*-dinaphthylurea, m.p. above 260° C. When it was heated with phthalic anhydride or *p*-nitrobenzoyl chloride and pyridine, badly discolored solutions were obtained from which no crystalline products could be isolated.

A mixture of Fractions 46, 47, and 48, totalling 27.7 gm., was heated with 18 gm. of tri-*n*-butyl borate at 100° C. and 30 mm. pressure for six hours 7.2 gm. of butyl alcohol, b.p. 49° C. (30 mm.), distilled. Unchanged reactants were removed at 100° C. and 1 mm. The residue (24.9 gm.) was steam distilled from 5 gm. of sodium hydroxide to give, after drying and redistillation, 12.3 gm. of colorless liquid boiling at 65° C. (3 mm.), n_D^{20} 1.4842, d_4^{20} 0.955, α_D +13.2°.

Sesquiterpene

Fraction I had properties within the sesquiterpene range. A solution of this material in two volumes of dry ether was saturated with hydrogen chloride at −30° C. *l*-Cadinene hydrochloride was formed in 56% yield. After crystallization from ethanol it melted at 118–119° C., $[\alpha]_D$ −37.9° (c = 5.50 in chloroform). An authentic sample of *l*-cadinene hydrochloride was prepared

*We are indebted to Dr. G. Wright and Mr. R. H. Meens of the University of Toronto for the X-ray diffraction examination of these compounds.

from the fraction of Cubeb oil boiling at 130–135° C. (10 mm.), α_D −13.7° C. This material had $[\alpha]_D$ −38.0°, and melted at 118–119° C. alone, or in admixture with the dihydrochloride from black spruce oil.

Higher-Boiling Fractions

Fractions II and III were yellow, extremely viscous oils which formed glassy solids on refrigeration. Their saponification numbers indicate 35 and 68% alcohols, and 20 and 18% esters respectively, assuming a molecular weight of 222 for the alcohol, and 264 for the ester.

A solution of 20 gm. of Fraction II in 80 ml. of hexane was percolated through 300 gm. of activated alumina in a column of 1.7 cm. diameter and 65 cm. height. The chromatogram was developed with 300 ml. of hexane and examined under ultraviolet light. A bright blue fluorescent band occupied the upper 2 cm., followed by a dark band occupying the center portion of the column. A thin band, showing bright green fluorescence, and a blue band were located near the bottom of the column. The column was sectioned and the separate bands were eluted with ethanol. Rechromatography of the eluates showed that no fraction was homogeneous. To date none of these components have been obtained in sufficient quantity or purity to permit characterization.

Results and Discussion

The approximate percentage composition of the essential oil from the needles of *Picea mariana*, as estimated from the distillation data, is as follows:

Terpenes: Santene, 2.5%; tricyclene, 1%; 1-α-pinene, 16%; *l*-camphene, 10%; *l*-β-pinene, 6.5%; myrcene, 3.5%; *d*- Δ^3-carene, 5%; *dl*- and *l*-limonene, 6.5%; terpinolene, 1%.

Alcohols: 1-Borneol, 1%; unidentified alcohol b.p. *ca.* 210° C. (760 mm.), 1%; unidentified alcohol b.p. *ca.* 120° C. (1 mm.), < 0.5%.

Ketones: *dl*-camphor, 1%.

Esters: *l*-Bornyl acetate, 37%; unidentified ester b.p. *ca.* 120° C. (1 mm.), < 0.5%.

Sesquiterpenes: Compound related to *l*-cadinene, 1%.
Residue and loss, 10%.

The presence of tricyclene in an essential oil is of interest as this is the first report of the occurrence of a tricyclic terpene hydrocarbon in nature. It has been reported (13) that tricyclene is present in camphene prepared by the dehydration of isoborneol. Since camphene is present in this oil it is possible that both compounds were formed by a similar dehydration of borneol in the living plant. At no time were conditions severe enough to effect this dehydration employed during distillation or subsequent examination of the oil.

In view of the low yield of camphor semicarbazone obtained, it is possible that other ketones may be present. The ketone components required more than a week to react completely with the hydroxylamine hydrochloride solution used in their analyses, and failed to react with sodium sulphite. Certainly no ketone which is more reactive than camphor is present.

The unidentified alcohol of Fractions 47 and 48 appears to be tertiary. It may be noted that the process of regeneration from the borate ester resulted in a product with a decreased dextrorotation. Since transesterification with tributyl borate is unlikely to result in racemization, the decreased dextrorotation of the regenerated product suggests that this material is contaminated with a more reactive, levorotatory alcohol, probably borneol.

It is unlikely that the black spruce sesquiterpene is *l*-cadinene, in spite of the fact that the dihydrochloride of *l*-cadinene was prepared from it in good yield. In view of the dextrorotation of this fraction, it is probable that this derivative was formed by the action of hydrogen chloride on some related sesquiterpene. Dextrorotatory copaene yields the *l*-cadinene derivative when treated with hydrochloric acid, but the high refractive index of Fraction I is not consistent with the presence of a high percentage of copaene. Briggs and Taylor (5) described a sesquiterpene from oil of *Dacrydium Kirkii*, with properties n_D^{25} 1.5055, d_4^{25} 0.9239, α_D^{30} +60°, from which *l*-cadinene hydrochloride was prepared in 60% yield. In spite of this dextrorotation they considered the fraction to consist mainly of *l*-cadinene.

Acknowledgments

This investigation was undertaken at the suggestion of Mr. R. N. Johnston, Chief, Division of Research, Department of Lands and Forests, Province of Ontario, and his colleagues, to whom we are also indebted for supplies of plant material. The essential oil was prepared by Mr. J. N. Brown and Dr. T. F. West. The investigation was supported by a grant from the Research Council of Ontario.

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SURFACE FILMS AND PARTICLE SIZE DETERMINATION OF POWDERS[1]

By Vincent R. Gray[2]

Abstract

It has been found possible to spread almost any powder on a water surface in a layer one particle thick and to study its surface pressure – area relation by conventional film balance techniques. A special sprinkler was developed for placing the powder on the surface, and flotation agents were adsorbed on particles which do not normally float. Fine particles needed extended outgassing and drying before they were sufficiently deflocculated. Although all films collapsed more or less readily on compression it was possible to define a point in the compression curve which represented a rigid film. The thickness of this film was a definite fraction of the mean particle diameter, measured by microscopic methods, the fraction varying with ease of agglomeration and with the shape of the particles. This method can be used for measurement of mean particle size and it possesses certain advantages over existing methods for many purposes.

Since the early experiments of Devaux (4), surface chemists have used finely powdered talc to indicate the state of surface films of organic compounds on water, or to indicate whether the surface is clean. No investigations seem to have been made, however [with the exception of some unpublished work by J. K. Roberts (8)], on the properties of the powder films themselves. The compressed areas of such films should provide a convenient means of measuring the mean particle dimensions of powders, particularly useful for those below the range of the simple microscope.

There are several obstacles which must be overcome in order to obtain a monoparticulate surface layer of a powder on water.

(1) The powder must float. A few solids, e.g., talc, corn starch, and sulphur, float spontaneously. Others may be made to float by adsorption of suitable substances which endow them with the necessary hydrophobic properties.
(2) The powder must be nonagglomerated or deflocculated in the film and therefore, presumably, before deposition.
(3) A suitable means must be found to spread it on the surface. This method must avoid loss of material as dust to the atmosphere, or powder sunk in the trough, for those particles which float with difficulty.

Experimental

A Cenco Hydrophil Balance was used for the surface pressure measurements. The platinum strips on that instrument were replaced by vaselined nylon monofilaments. Since the mica pressure barrier has a tendency to rotate, as it is held only in the middle, two vertical glass forked struts were hung from

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the horizontal torsion wire, the prongs of the fork dipping into the trough on each side of the barrier. Initial experiments were carried out on talc. The first problem was to deposit the powder on the surface without flocculation or loss in the air or in the water.

The conventional "pepper pot" type of apparatus tends to deposit fairly large agglomerates of talc on the surface, and furthermore some is lost as dust or sinks.

It was found that there is a tendency for agglomerates of particles to spread on the surface. This tendency is not complete, as some smaller agglomerates remain, but it means that for powders that have been fairly well deflocculated it is not too difficult to achieve a surface layer which is largely composed of single particles.

After experimentation with various types of devices for spreading the powder, the sprinkler depicted in Fig. 1 was evolved. It consists of a fine copper gauze set (by means of paraffin wax) in a wide glass tube closed by a

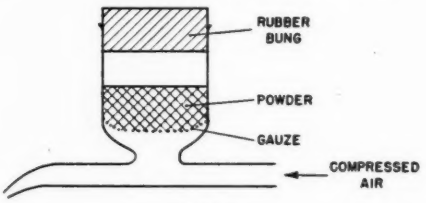


FIG. 1.

rubber stopper and joined at right angles to a narrower tube. The dimensions are about 1 in. by 2 in. When the sprinkler is tapped gently the powder falls through the copper gauze, and it is carried onto the surface by a compressed air jet through a narrowed nozzle. The force of the air jet is adjusted to give the best spreading conditions, and quantitative transfer of solid to the liquid surface. The amount of powder transferred is determined by weighing the sprinkler before and after the sample has been spread.

It should be possible to spread powders by transferring an aliquot from their uniform suspension in benzene to the water surface. Considerable difficulty may be encountered, however, in preparing a uniform suspension of sufficient concentration. This difficulty and the attack of the benzene on the wax coating at the trough edges make the method impracticable.

After the talc experiments a series of powders were studied as typical of various kinds of behavior and difficulty. They were corn starch, potato starch, iron oxide, and bentonite. It was found possible to cause all of these to float where necessary by adsorption of suitable paraffin chain compounds. An additional powder, sodium chloride, typified a group which could not be studied, as no adsorbed substance tried out would cause it either to float or to avoid its dissolution in the water.

The mean size of all the particles studied was found by microscopic examination. For those of appreciable size ($> 5\mu$) a random sample of particles (*c.* 100) was measured by means of a micrometer eyepiece, and the mean dimension found by arithmetic averaging. This was used for corn and potato starch, and for the larger talc fractions.

For small particles a weighed amount of powder was dispersed in a known volume of a nonvolatile viscous medium—mineral oil plus a small amount of oleic acid being used.

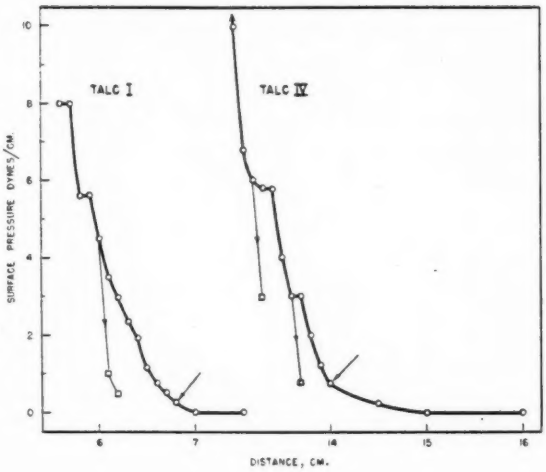


FIG. 2.

After shaking well, a representative drop of the suspension, about 2 mgm., was weighed out on a clean microscope slide on a microbalance and the drop covered by a coverglass of known area. The number of particles in a field of known area was counted under the microscope by the use of the micrometer eyepiece for a representative selection (about 30) of portions of the slide. Thus the mean number of particles per unit volume of solid n could be calculated with a knowledge of the density. The "mean particle dimension" was then taken as the reciprocal of the cube root of n.

As few of the particles investigated were below the limit of resolution of the microscope, other methods of measurement were not necessary. Several approached this limit, however, and caution was necessary to pick out all particles in the field.

As the counting method gives a mean dimension which depends on the cube root of the number of particles counted it is more accurate than the direct method, providing the dispersion is uniform.

It was found possible to remove the powder films from the trough by dipping a clean glass slide in the water. This technique is similar to that employed with monomolecular films, except that the film adheres to the slide only on the upward journey and it can only be removed from the water by putting the slide under the film at an angle and bringing the slide up beneath it. One layer only can be obtained. This layer could be examined under the microscope when dry and the nature of the film shown. Thus it was possible to observe when the powder was completely spread and the way in which the particles packed together. Typical photomicrographs are shown in Figs. 6–12.

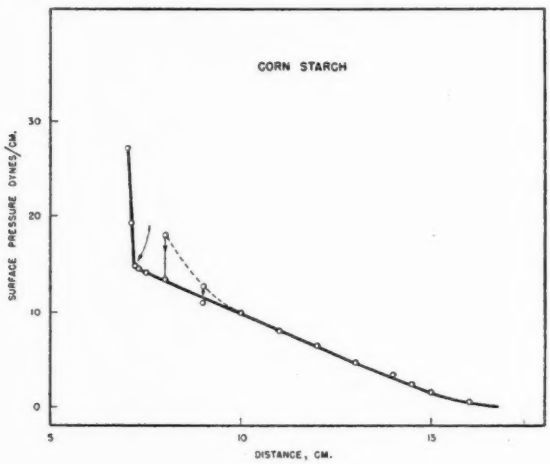


FIG. 3.

Floatability of Powders

All powders studied, with the exception of talc and corn starch, sank when placed on the surface of water. It was, therefore, necessary to find a means of causing them to float.

It has been pointed out by Wark (9) that almost any polar organic substance, and especially those containing long hydrocarbon chains, may behave as flotation agents. The main object here was to find substances which were adsorbed sufficiently strongly on the powder to render it hydrophobic enough to float when applied to the water surface. This is a more rigorous requirement than the ultimate adhesion to a rising stream of air bubbles involved in flotation. Preliminary work showed that fatty acids seemed to give reasonably good results. It was felt that the effect of the surface active substance might interfere with the interpretation of the behavior of the powder, and two possible methods of obviating the difficulty were devised. One was to employ an adsorbent which dissolved in the substrate. Caproic acid is a good example of such a substance. This method was not too successful, as solution was usually

very slow owing to diffusion, and enough fatty acid usually remained in the film to give an appreciable surface pressure. The other method was to use a substance which gives a constant surface pressure over the whole or part of its range. "Piston oils" such as castor oil are the best examples here, and, as fatty acids like oleic behave as a piston oil when in excess, most experiments were carried out under these conditions, i.e., with a sort of "base line" pressure given by the oil, upon which was superimposed the effect of the powder.

Some experiments were carried out with commercial wetting agents, which below their micellar concentration in water behave as flotation agents, but as they were no better than fatty acids, investigations were not carried further.

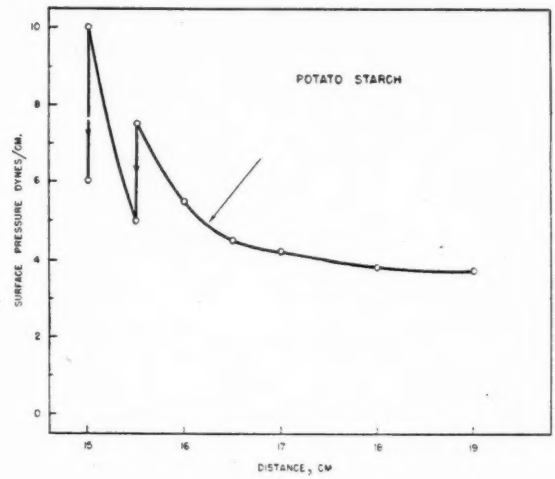


FIG. 4.

It was soon found that adsorption of fatty acids on powders was in few cases as thorough as on the oxides (5, 7). With potato starch, for example, the powder would float only after it had been in a benzene solution containing 0.2% caprylic acid. Bentonite, the most difficult to float of the substances studied, required immersion in a 4% castor oil solution. Even with oxides an excess of adsorbent appeared advantageous, as it assisted surface dispersal of agglomerates and provided an almost constant surface pressure throughout the compression. The procedure for powders which required adsorption was as follows. The powder was at first dried in an oven or a vacuum desiccator. It was then deflocculated by ball milling or by vigorous stirring in dry benzene with a little fatty acid, filtered, and dried in a vacuum desiccator, and then transferred to a high vacuum apparatus at 10^{-2} mm. for further drying overnight. After being put in the solution of adsorbent, of sufficient concentration to cause it to float on water, it was filtered after a few hours, dried once more in the vacuum desiccator, and stored in a tightly stoppered bottle.

An attempt was made at one stage to make a surface filter, that is to say, a one-dimensional membrane which could separate the comparatively large particles of a powder from the smaller molecules of surface active materials. It was soon realized that the usual two-dimensional membranes, such as filter paper, were useless because of capillary rise. Eventually a strip of brass with a series of vertical slits cut into it was mounted on a gap in a horizontal barrier. Owing to the high viscosity of surface films and the ease with which holes became blocked by particles of powder, the width of the slit necessary to give appreciable flow of fatty material also permitted powders to pass through. Though a measure of separation was achieved in a few instances the method was abandoned when it became clear that the presence of fatty materials is no barrier to the measurement of particle size of the powders.

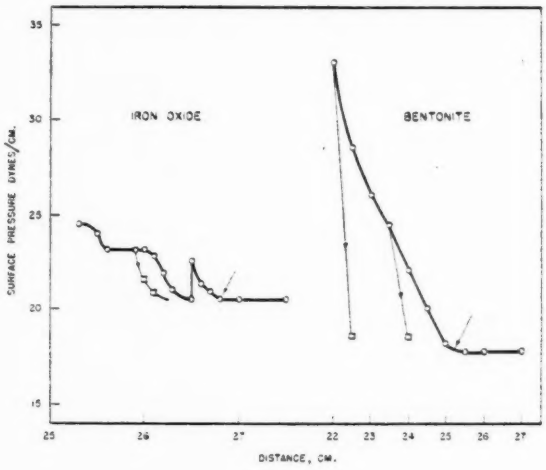


FIG. 5.

Agglomeration and Moisture

Agglomeration in fine powders is particularly pronounced in the presence of moisture. All powders were, therefore, thoroughly dried. However, it was found that the finer powders still agglomerated appreciably and also clogged the gauze in the sprinkler. It was, therefore, necessary to observe the precautions used by Harkins and Gans (4) and evacuate the powders in a high vacuum, heating where possible, for many hours. The sprinkler was kept in a desiccator and the air jet was led through a drying tube. Some agglomeration persisted even under these conditions but it was not usually detrimental to the measurements.

Results

Talc

Some finely powdered talc was fractionated by repeated sedimentation in water. The smallest fraction was dry ball milled to make it more uniform.

The compression curve of talc samples applied to the water surface was studied. The curves showed the following features:

1. There was a zero surface pressure until the powder film appeared to fill the available free surface, whereupon the pressure began to rise, first gradually, and then steeply.
2. The pressure–area curve was in general not reversible, though a film which had been kept compressed for some time was fairly stable on compression and decompression and had a very high compressibility. The reversal curve taken from a high pressure, say 10 dynes per cm. to lower pressures, was always much steeper than the compression curve and it was almost a straight line.

The nonreversibility of the compression curve was probably due to one or all of the following factors:

(*a*) "Compacting" of the film, spaces remaining free at first being filled by compression.

(*b*) Tilting and upturning of anisometric particles so that their least dimension in the film is replaced by a greater thickness. This should be at least partially reversible and is probably the main factor determining compressibility in decompression curves.

(*c*) Agglomeration of particles to give a polyparticulate layer.

As it seems difficult to isolate all these effects the area of the film at the position where the pressure first began to rise was taken as a basis for particle size measurements. This point is analogous to the "gel point" of protein films, and it can be determined accurately by an analogous method, namely, by taking the point of maximum curvature of the surface pressure – area curve (3). It could be tested also by the method used with proteins (2). It was the point where the film first showed resistance to a light air jet blown on the surface.

The largest fraction "I" was dried by ignition. Pressure behavior of the film is shown in Fig. 2 and a compressed film in Fig. 8. Some of this fraction was retained on a 200 mesh Tyler sieve. This had the effect of isolating mainly the needle-shaped particles (Fig. 9). Both these fractions were difficult to measure as they were anisodimensional and disperse, the second fraction to a greater extent than the first, but it was evident (Table I) that the needle-shaped particles in Fraction II gave a decreased film thickness and an increased mean particle dimension. This shows that the needles have their small dimension in the surface, and that they also form a more open network at the point where they first resist compression. Fig. 9 represents a highly compressed film where some agglomeration has occurred.

The finer talc fractions were evacuated for 15 hr. while heated. By this means fairly well spread films, shown in Fig. 2 and Figs. 10 and 11, were obtained.

TABLE I

COMPARISON OF COMPACTED FILM THICKNESS AND PARTICLE SIZE FOR VARIOUS POWDERS

Substance	Treatment	Adsorbent	Film thickness, μ	Mean dimension (microscope), μ	f	Remarks
Talc I	Dried	None	8.00	c 11.4	1.42	I and II—very disperse, so inaccurate count
II	"	"	4.31	c 20	c 4.6	Sample I passes through sieve to isolate needle-shaped particle
III	"	"	2.18	2.32	1.06	Film somewhat agglomerated
IV	Evacuated	"	0.58	1.36	2.35	Well spread
V	"	"	0.65	1.55	2.38	Well spread
Corn starch I	Dried	None	6.66	8.91	1.34	Well spread, particles repel
Corn starch II	Extracted 3 days and dried	"	6.43	8.65	1.34	Well spread, particles repel
Potato starch I	Dried	0.4% caproic acid	10.4	29.6	2.84	Readily agglomerated on compression, spread well
Potato starch II	Evacuated	0.2% caprylic acid	10.3	23.6	2.28	Readily agglomerated on compression, spread well
Iron oxide I	Dried	0.5% caproic acid	.765 – 1.05	1.10	<1.44	Some agglomeration
Iron oxide II	Evacuated	0.5% caprylic acid	0.60	0.78	1.30	Well spread
Bentonite I	Evacuated	4% castor oil	0.48	1.15	2.42	Spreads slowly, agglomerates on compression

To indicate the reproducibility of the values for the mean thickness of the film at the solidification point the following values obtained with talc fraction IV are typical.

The number of grams of material deposited, divided by the number of centimeters along the scale corresponding to solidification point, were:

0.00239 gm. per cm, 0.00216, 0.00225, 0.00265, 0.00281, 0.00248.

In this case more weight should be given to the lower values, as all the errors tend to increase the answer, therefore 0.00232 is taken as the mean of the four lowest values, giving a value of the mean thickness of 0.58 μ. Accuracy here is of the order of 5% only but it can be improved by more determinations.

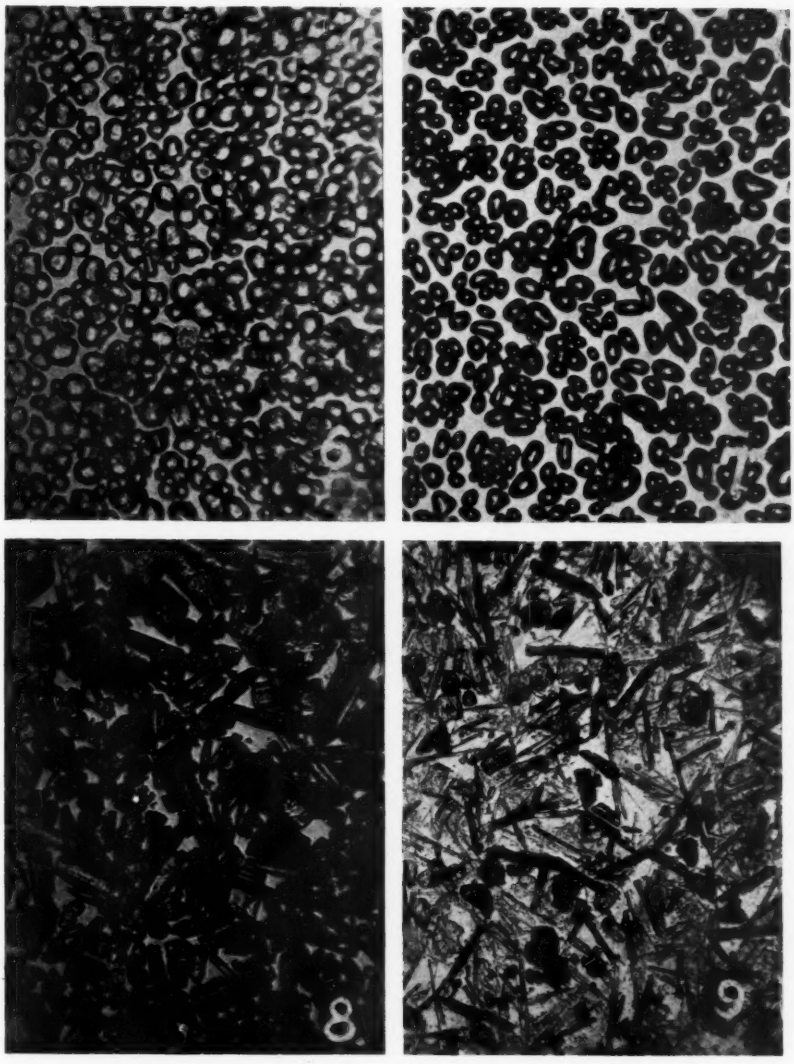


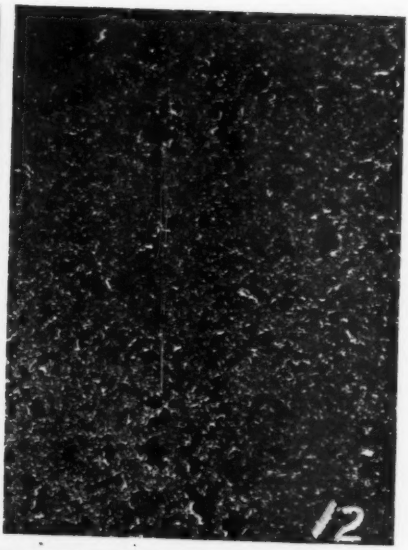
FIG. 6. *Corn starch II.* ×290.
FIG. 7. *Potato starch II.* ×122.
FIG. 8. *Talc I.* ×122.
FIG. 9. *Talc II.* ×45.

Corn Starch

A specimen of "Casco Ground" corn starch was fractionated somewhat by sedimentation. As the sample appeared to be remarkably uniform in size, fractionation was not thorough. The washed material was dried overnight in a vacuum desiccator. It floated very well, but it had a quantity of fatty material in it which spread on the water surface. A sample was therefore cold-extracted in a modified Soxhlet apparatus for three days with dry dioxane. Some fatty material still remained, but this was of utility, as further extraction gave material which showed a tendency to sink. The starch was sprinkled on the surface in the same manner as the talc, and pressure–area curves were plotted. These are shown in Fig. 3. They differed from those of talc in that the compression of the fatty material was involved. A further feature observed was a partially reversible adsorption of the film of fatty material on the corn starch. Fast compression gave much higher pressure values than slow compression, and they fell in the course of time to the slow compression values. Also, fast decompression gave a lower pressure which rose slowly to the slow decompression value. Periodic compression and decompression gave a hysteresis curve. This shows that a highly compressed fatty film adsorbs on the corn starch and that it leaves the starch for a water surface with a dilute film. The best curves for corn starch were therefore obtained by slow compression. They then resembled the curves for talc, and the point of maximum curvature was taken as a measure of a condensed film. Fig. 6 shows a slide of withdrawn film. The photograph does not exactly reproduce the appearance of the compressed film, as (i) some pressure is lost when the film is transferred to the glass slide, and (ii), on drying, the individual particles tend to agglomerate. However, it may be seen that the film is very well dispersed and that agglomeration occurs hardly at all—in contrast to all other materials.

Potato Starch

A specimen of potato starch was fractionated by repeated sedimentation in water. The dried powder was made to float by immersion in a solution of 0.4% caproic acid in dry benzene and another sample by 0.2% caprylic acid in dry benzene. The films produced were nonreversible to pressure. The starch granules agglomerated and sank readily on compression. However, it was still possible to obtain a "compacted area" as before. The photomicrograph in Fig. 7 shows the starch granules clustered into small groups. This is an artifact produced on drying, as the film as withdrawn was compressed, and therefore compact. The comparatively large free area indicates that the original film possessed an open network structure, which gave small groups on drying. This is due to the strong agglomeration tendency of the potato starch with adsorbed fatty acid (as contrasted with its behavior without adsorbent) which gives an open network structure on compression which is analogous to the high sedimentation volume given by flocculating solids in suspension (1, 6). The ratio f of particle size to film thickness is very much



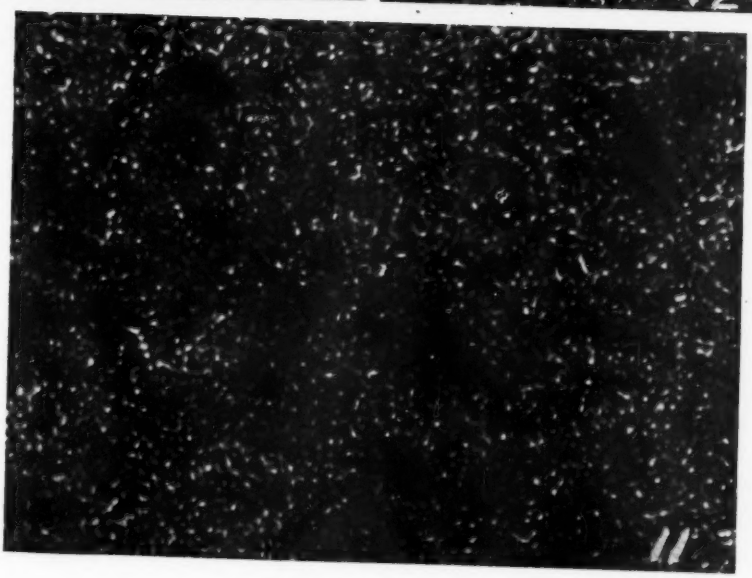


FIG. 10. *Talc III.* ×*360.*
FIG. 11. *Talc V.* ×*950.*
FIG. 12. *Iron oxide* II. ×*263.*

higher (*c.* 2.5) for potato starch than for corn starch (1.34), and as the particles of both are almost spherical this agglomeration effect must be the main reason for the difference between them.

Iron Oxide

A specimen of iron oxide was ball milled in dry benzene with 0.5% caproic acid or caprylic acid for several days. It was dried in the high vacuum apparatus at 10^{-2} mm. for 24 hr. but not heated, as it sinters readily. Lesser amounts of fatty acid were necessary for floating, but excess is not deleterious.

The particle size was of the order of that of the smallest talc fraction.

The films (see Figs. 5, 12, 13) gave an opaque red compact area. The film agglomerated readily and so the first evidence of a sudden increase in pressure was taken as the compact area, as before. f was of the same order of magnitude as for corn starch, which confirmed the impression from microscopic examination that the particles are almost spherical.

Bentonite

A sample of "Super Filtrol" was ball milled with dry benzene and 4% castor oil for several days, filtered, dried, and evacuated in high vacuum at 10^{-2} mm. for several days. It was not heated, as even 100° C. caused it to turn gray. The material floated with difficulty and a small percentage of material (*c.* 1 to 2%) was lost by sinking.

The film as first sprayed onto the surface contained much agglomerated material but it was found that this was largely dispersed after half an hour when measurements were made. The film under compression was almost transparent and agglomerated readily but measurements were made as before. A typical curve is shown in Fig. 5. To illustrate reproducibility for this, the most intractable of the materials studied, the following successive values for film thickness are given—0.516μ, 0.453, 0.476, 0.492, 0.506.

Particle Size Measurement From Surface Pressure Curves

The first necessity for particle size measurement is to select a point on the surface pressure – area curve suitable for giving a reproducible mean film thickness. The point eventually chosen was the first position of maximum curvature near the region where the film appears compact visually. This point is indicated by an arrow on all curves shown. It was usually quite sharply defined, even when a surface active compound with an irregular compression was present.

Its actual determination may be confused if the collapse point of the surface active additive occurs near the compression point of the solid powder. This actually happened with corn starch, and two discontinuities may be seen in the graph. The second sharper kink is evidently due to the close packed

starch particles. Slow compression of the film allowed the surface active agent to readsorb on the starch granules and appeared to be a desirable procedure. The solidification point may also be masked if the powder floats poorly or agglomerates readily. These are usually slow processes, however, and rapid compression of the film will show up the point of maximum curvature before collapse takes place. Since the phenomena produce similar compression curves it is necessary to distinguish between them by careful visual observation.

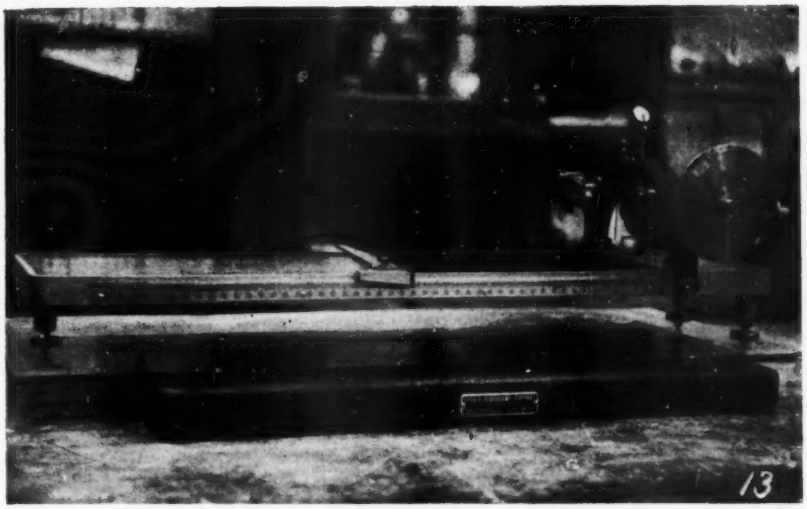


FIG. 13. *Trough with compressed film of iron oxide (between barriers).*

All the films displayed collapse phenomena at quite low pressures (*c.* 3 to 4 dynes above pressure of adsorbent), being strongest where the agglomeration tendencies were greatest. At first, therefore, some doubt was felt as to the point to be taken for film thickness measurements. Talc films (medium particle size in particular) on compression beyond the first pressure rise settle down to a film which is quite stable for 10 min., and which will stand a high surface pressure, *c.* 10 dynes, without collapse. However, the area was not reproducible and also it was arbitrary, depending on speed of compression and time elapsed before a reading was taken. The first rise in pressure was much better defined; it represented a true first solidification of the film. This solidification could be demonstrated by the resistance of the film to a light air jet, with no dependence on arbitrary factors.

The ratio f of the mean particle dimension to the film thickness as here determined depends on the shape of the particles and on the ease with which they agglomerate on the surface. For corn starch, where the particles are almost spherical and repel one another on the surface, f is equal to 1.34.

The particles of iron oxide behave similarly to corn starch and give a value of f which is close to 1.34.

Where the particles agglomerate readily, a higher value for f is obtained, even when the particles are almost spherical, as with the potato starch, for which f is about 2.5. Since agglomerating particles form a more open structure the f value is higher.

Anisodimensional particles also increase the value of f. Not only do they lie with the least dimension in the surface but they form a more open network structure.

It would seem that this method of particle size measurement has several advantages over existing methods.

(*a*) It does not require elaborate apparatus—merely a film balance and drying equipment.
(*b*) It gives a large and therefore representative sample average.
(*c*) Apart from possible initial preparation of the powder it is very rapid—15 min. should suffice for an experienced operator.
(*d*) A reproducible and readily measured average size for a highly polydisperse powder may be found. Few other methods possess this advantage.
(*e*) It can be applied over a very wide range of particle size—about 1 mm. to 10^{-5} mm. or less.

Its disadvantages are:

(*a*) For fine powders, elaborate treatment is often needed to deflocculate the powder. This drawback is, however, common to most other methods, e.g., gas or liquid adsorption methods, permeability.
(*b*) An empirical factor must be established for each type of powder to convert film thickness to mean particle diameter. For roughly spherical, not strongly agglomerating, particles, this factor is about 1.34. Where surface agglomeration occurs or particles are needle shaped or platelike it may rise to 3 or 4.
(*c*) Only the number average particle size is measured and no idea of size distribution, shape factor, specific surface, etc., can be given.
(*d*) The accuracy and reproducibility is not usually better than 2 to 5%.

However, it is felt that this method can be a useful tool in particle size measurement, particularly in routine control of atmospheric and industrial dusts. Improvements, such as a better kind of sprinkler (e.g., a dry "colloid mill") or the use of a mercury surface instead of a water surface, might do much to remove its present objections.

Acknowledgments

I wish to extend my thanks to Dr. I. E. Puddington for his direction and useful advice. I am indebted to the National Research Council of Canada for a Postdoctorate Fellowship.

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THE DENSITY OF WATER SORBED ON CHARCOAL[1]

By H. L. McDermot[2] and N. G. M. Tuck[3]

Abstract

The apparent volume of water sorbed by a zinc chloride activated charcoal has been measured over the entire range of relative pressures, employing an apparatus especially designed to eliminate carry-over of water vapor into the sorption cell. The apparent volume has been found to be consistently greater over the entire sorption isotherm than the normal volume of an equal weight of liquid water, and it tends to be slightly higher on desorption than on adsorption. The results are in qualitative agreement with those of Wiig and Juhola and in marked disagreement with those of Morrison and McIntosh.

Introduction

The various theories of sorption are all derived from the measurement of sorption isotherms and heats of sorption. Although these theories contain postulates, implicit or direct, concerning the nature of the sorbed film, few properties of the sorbate have been measured directly. One property, which has received some attention in recent years, is the apparent volume of the sorbate as measured by the displacement of helium.

Morrison and McIntosh (3) measured the sorption isotherm and the apparent volume of water sorbed on four samples of activated charcoal. The isotherm was determined by weighing the cell containing the charcoal before and after exposure to sulphuric acid – water solutions of known vapor pressure. To measure the free volume of the sorption cell, a mixture of water vapor at the equilibrium pressure and helium at a much higher pressure was expanded from a known volume into the cell; the free volume of the cell was computed from the change in the partial pressure of the helium, assuming the water vapor to be at the equilibrium pressure throughout the cell-expansion system. The apparent volume of the sorbed water is the difference in free volume of the cell before and after the addition of a known weight of water. The apparent volume so obtained was low initially but increased rapidly with increasing sorption, then remained approximately constant at a value slightly below the normal liquid volume until saturation, where it increased abruptly. Severe criticism has been leveled at the work of Morrison and McIntosh (3) by Emmett (1, pp. 91-92) and by Wiig (5, p. 564). Emmett believes that low apparent volumes may be due, in part, to contamination by sulphur trioxide from the sulphuric acid – water solutions. Wiig questions the results on the grounds that the calculated partial pressure of the helium after expansion is in error owing to carry-over of water vapor from the expansion chamber to the

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sorption cell; since a portion of the water vapor carried over into the sorption cell would be sorbed by the charcoal, the computed partial pressure of the helium would be too low.

Tuck, McIntosh, and Maass (4) measured the apparent volume of diethyl ether and carbon tetrachloride sorbed by an activated charcoal, using an apparatus and technique very similar to that of Morrison and McIntosh (3). They showed experimentally that in their apparatus carry-over of vapor into the sorption cell did occur.

Wiig and Juhola (5) have measured the apparent volume of water sorbed by various charcoals, using a constant pressure method and measuring the free volume directly. They found the apparent volume to be consistently higher than the normal liquid volume. Although the results of Wiig and Juhola (5) were not published until after the completion of the experimental work reported here, Wiig's criticism of the results of Morrison and McIntosh (3) were known to us (4, p. 27). It was because of this criticism and the experimental detection of vapor carry-over by Tuck, McIntosh, and Maass (4) that it was decided to repeat the measurement of the apparent volume of water sorbed by charcoal, using an apparatus designed to eliminate the carry-over of vapor into the sorption cell during the measurements of the volumes by the expansion of helium.

Experimental

The charcoal used was a zinc chloride activated material designated as CWSN178B-2. Samples of the charcoal have been used by other workers in this laboratory (2, 3, 4). Its properties are as follows:

TABLE I

Density in helium, gm./cc.	1.88 1.91 (3) 1.96 (2)
Density in water, gm./cc.	1.74 1.74 (3) 1.71 (2)
Area m.²/gm.	1840 (2)

The apparatus consisted principally of a sorption cell (*A*), containing 33.88 gm. of activated charcoal, connected through a short length of capillary tubing and a two-way stopcock (*O*) to an expansion bulb (*B*). The expansion bulb was connected at the bottom by a length of capillary tubing to a mercury reservoir (*C*). This bulb (*B*) was accurately calibrated from the mark (*P*) on the capillary to the two-way stopcock (*O*), and had a volume of 110.68 cc. Mercury from the reservoir (*C*) could be transferred to or from the expansion bulb (*B*) by varying the pressure in the reservoir. The constant volume manometer (*F*), provided with a reflecting glass scale, enabled estimation of

pressures in the sorption cell (*A*) or in the manifold (*G*) to 0.1 mm. The section of the apparatus enclosed in the dotted lines was immersed in a thermostat maintained at 24.93° C.

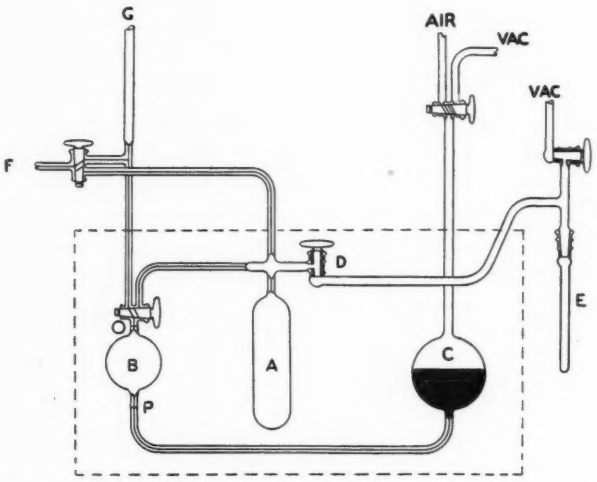

FIG. 1. *The apparatus used for measuring the density of the adsorbate.*

The volume of the free space within the sorption cell was determined as follows:

1. Helium was introduced from the manifold (*G*) through the stopcock (*O*) into the expansion bulb (*B*). The level of the mercury in the expansion bulb was set at the mark (*P*) and the pressure was read on the manometer (*F*). The stopcock (*O*) was then closed, the manometer (*F*) evacuated and opened to the cell-expansion system.

2. Helium was expanded slowly from the bulb (*B*) into the cell (*A*) while maintaining the mercury level at (*P*). The resulting pressure was read.

3. The helium was then displaced from the bulb (*B*) into the sorption cell and the pressure again noted.

The volume of the free space could then be calculated from the known volume of the expansion bulb and any two of the above pressures; in practice, pressures 1 and 3 were employed.

Prior to sorption measurements the charcoal was degassed by heating to 200° C. and evacuating until the pressure in the vacuum line fell to less than 10^{-4} mm. Using this technique for cleaning the surface of the charcoal, no change in the volume of the free space was detected after many sorption cycles. The apparent density of the sorbed water was measured in the following way. A weighed quantity of water was introduced into the thimble (*E*) and degassed by alternated freezing, evacuating, and thawing. The water was allowed to

sorb on the charcoal, and time–pressure readings were taken until the pressure became constant. When equilibrium was established, the free space was measured as described above except that Step 2 was eliminated. The apparent density was calculated from the known weight of water and the measured change in the volume of the free space.

During the course of the measurements of the apparent volume, a small drift in the final pressure reading was observed. The pressure increased approximately 0.5 mm. over a period of two hours, and then became constant. The constant value was employed in the calculation. This drift can be explained as follows. When helium is expanded into the sorption cell the water vapor is swept toward the bottom of the cell, momentarily increasing the partial pressure there, and causing the water vapor there to sorb. Gradually the water vapor becomes uniformly distributed throughout the cell, and desorption occurs, causing the pressure to increase slowly.

Results

The sorption isotherm is plotted in Fig. 2; it is S-shaped and exhibits limited hysteresis from $P/P_0 = 0.5$ to $P/P_0 = 0.9$. The values of the apparent volumes of various amounts of sorbed water are listed in Table II and plotted as apparent volume versus weight sorbed in Fig. 3 and as the apparent density versus weight sorbed in Fig. 4. The apparent volume is greater over the whole course of the isotherm than the volume of an equal weight of water in the liquid state, and, further, it is slightly higher on desorption than on adsorption.

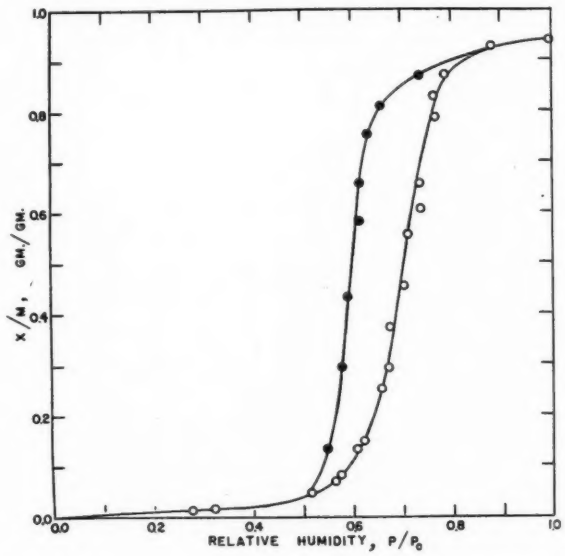

FIG. 2. *The sorption isotherm of water on charcoal at 25° C.:* ○, *adsorption;* ●, *desorption.*

TABLE II

APPARENT VOLUME OF WATER SORBED ON CHARCOAL

Weight of water, gm./gm. of charcoal	Volume of sorbed, water cc./gm. of charcoal
Adsorption	
0.0499	0.0548
0.0714	0.0752
0.1435	0.158
0.254	0.268
0.293	0.307
0.374	0.398
0.454	0.485
0.555	0.589
0.607	0.644
0.767	0.812
0.828	0.862
0.926	0.975
0.941	0.985
Desorption	
0.867	0.922
0.810	0.867
0.655	0.705
0.433	0.468
0.139	0.151

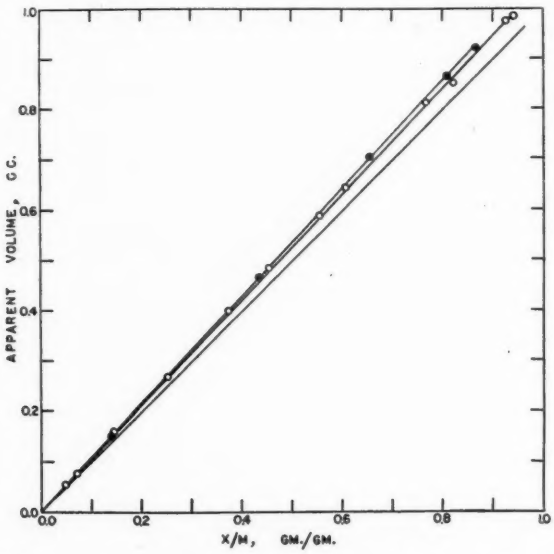

FIG. 3. *The apparent volume as a function of the weight of sorbed water:* ○, *adsorption;* ●, *desorption.*

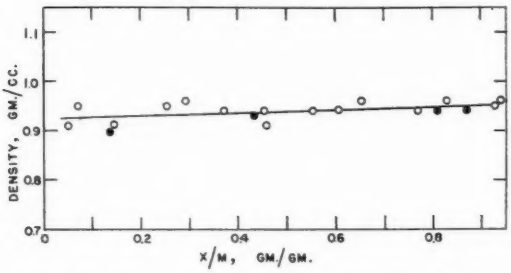

FIG. 4. *The apparent density as a function of the weight of sorbed water:* o, *adsorption;* ● *d, desorption.*

It is at once apparent from a comparison of the curves in Fig. 3 with those published by Wiig and Juhola (5, p. 565) that the two sets of results are in excellent qualitative agreement even though the measurements were made on different samples of charcoal, using different techniques. However, the curve shown in Fig. 4 differs markedly from the corresponding curve for the same charcoal that was published by Morrison and McIntosh (3, p. 144). The value obtained here for the apparent density of water sorbed at saturation does agree with that found by Morrison and McIntosh (3). This completely vindicates the criticism of Wiig and Juhola (5, p. 564), since the error due to water vapor carry-over and subsequent sorption in the apparatus used by Morrison and McIntosh (3) would be nil at saturation.

Acknowledgments

The authors wish to express their appreciation to the Defence Research Board for financial assistance and to Dr. O. Maass for his continued interest in this project.

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VISCOSITY STUDIES OF A BRANCHED POLYSTYRENE COPOLYMER[1]

By O. J. Walker, Jr.[2] and C. A. Winkler

Abstract

The viscosities in dilute toluene solution of fractions of polystyrene prepared at various temperatures and catalyst concentrations were found to conform to the relation $\eta_{sp}/C = [\eta] + k'[\eta]^2$, where $k' = 0.38$. When styrene was copolymerized with quantities of divinyl benzene insufficient to cause gelation the viscosity–concentration relation changed, resulting in values of k' from 0.50 to 0.84. It was concluded that the polystyrene molecule is normally linear.

Introduction

The viscosity of polymer solutions has been studied both theoretically and experimentally to obtain information about the size and shape of high polymer molecules. For many polymer–solvent systems the relation between viscosity and concentration, in dilute solutions, is expressed by the Huggins–Kraemer equation (14, 15, 16)

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 C,$$

where η_{sp} is the specific viscosity, $[\eta]$ the intrinsic viscosity, C the polymer concentration (grams per 100 ml. solution) and k' a constant. The constant k' has been designated a specific solvent–solute interaction constant, or shape factor (1) and is believed to be a function of the configuration of the polymer molecule in solution.

Theoretical considerations by Debye and Bueche (7) have shown that the value of $[\eta]$ should be less for a branched or cross-linked polymer than for a linear polymer of the same molecular weight, while Simha (22) has predicted, also on theoretical grounds, that the value of k' should increase with the degree of cross-linking or branching, a prediction for which there is some experimental evidence. The highest molecular weight fractions of some diene polymers, such as Neoprene (17) and GR-S. (13, 26), show greater values of k' than the lower molecular weight fractions. Also, polyvinyl acetate exhibits an increasing k' value as the gel point is approached (18), while the k' values for amylopectin (branched) and amylose (linear) are 1.47 and 0.58 respectively (23). On the other hand, k' for polystyrene in toluene has been reported to decrease from 0.42 to 0.21 as the temperature of polymerization was increased (2), the decrease in k' being attributed to more extensive branching. Spencer and Boyer (24) have claimed that k' is a function of the length heterogeneity of a polymer fraction, but this view is opposed by Davis (6).

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In the studies mentioned above, the polymers were not strictly comparable, owing to differences in composition or chain length. The greater tendency for longer chains to coil (21) might account for some of the observed changes in k'. In the present study, linear and branched polystyrenes of similar composition and viscosity have been prepared and their rheology examined, in an effort to obtain more reliable information about the significance of k' values. It appeared that the presence of small amounts of divinylbenzene (D.V.B.), an effective cross-linking agent (25) of structure similar to styrene, should provide an unequivocal means of introducing branches into polystyrene without significantly changing the composition. Some studies have been made on the effect of bifunctional groups on the molecular weight distribution of polystyrene (27) and on the properties of the gels thus formed (4), but no study of the viscosity of the branched copolymers has been reported.

Experimental and Results

Materials

Styrene, obtained from Polymer Corporation, Sarnia, was freed from inhibitor and water by vacuum distillation. The middle fraction was collected and stored for a maximum of two days at 0° C.

Divinylbenzene (D.V.B.), supplied by Polymer Corporation, was stored at 0° C. until needed. It was stated to be a 40% solution in ethylvinylbenzene.

The benzoyl peroxide, toluene, and methanol used were all Merck C.P. grade.

Preparation and Examination of Polystyrene Fractions (no D.V.B. present)

Styrene was bulk polymerized with 0.02%, 1.00%, and 5.00% benzoyl peroxide respectively to about 50% conversion at 60° C. The polymer was separated from catalyst and residual monomer by two precipitations from toluene with methanol. The sticky mass was thoroughly kneaded under methanol with a glass rod after each precipitation.

Approximately 60 gm. of polymer was dissolved in toluene and fractionated roughly in a 4 liter separatory funnel by the judicious addition of methanol. Head fractions were diluted to a concentration of less than 1% with toluene and refractionated to obtain two or three high molecular weight fractions, each weighing 2 to 5 gm.

Other polymerizations were made at 120° C. with 0.02% benzoyl peroxide and at 180° C. with no catalyst and with 0.02% benzoyl peroxide. Small sealed glass tubes were used for these preparations to obtain rapid temperature equilibrium with the surrounding bath, the contents of several tubes being combined and fractionated as described above.

Viscosities were measured in duplicate at five low concentrations (less than 1%) in two Ubbelohde type viscometers rigidly supported in a constant temperature bath at 25.0° C. The viscometers were equipped with a large

reservoir to permit dilution in situ. The flow times of pure toluene were checked frequently and did not change throughout the work. Kinetic energy correction factors calculated from the flow times of benzene and of water were negligibly small.

Efflux times were checked to ± 0.1 sec. with an electric timer. Relative viscosities (the ratio of the flow time of the solution to that of the pure solvent) (5, 20) were accepted when the agreement between the two viscometers was ± 0.001 unit or better. To attain this precision it was necessary to filter the polymer solutions through a fine sintered glass crucible and to dilute with distilled toluene from calibrated pipettes. The concentration of polymer was determined gravimetrically by evaporating 40.0 ml. of the solution to constant weight.

The plots of η_{sp}/C against C were found to be straight lines. The logarithms of the slopes of these lines are plotted against the logarithms of the intercepts in Fig. 1. All the points are seen to be close to a straight line of equation,

$$\log_{10}(\text{slope}) = \log_{10} 0.38 + 2.0 \log_{10}[\eta],$$

from which it can be deduced that

$$\eta_{sp}/C = [\eta] + 0.38\,[\eta]^2\,C.$$

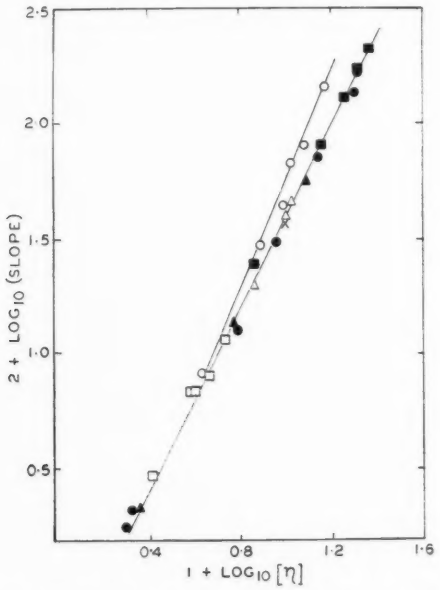

FIG. 1. *Correlation of slopes and intrinsic viscosity of polystyrene. All are fractions of bulk polymerized polymer in toluene, except where noted.*
● *60° polymer,* △ *120° polymer,* □ *180° polymer,*
× *Monsanto "Lustron",* ▲ *60° polymer, unfractionated,*
■ *Emulsion polymerized [Goldberg et al., Ref. (12)],*
○ *Emulsion polymerized in methyl ethyl ketone [Goldberg et al., Ref. (12)].*

The data of Goldberg, Hohenstein, and Mark (12) for emulsion polymerized polystyrene in toluene and in methyl ethyl ketone have also been plotted in Fig. 1. The data for their polymers in toluene are in good agreement with the above relation, but those for polymers in methyl ethyl ketone show considerable deviation, to which further reference will be made.

Polystyrene in toluene appears to conform to the Huggins–Kraemer equation. Table I shows the values of k' for the various fractions as well as for some unfractionated material, calculated on this assumption.

TABLE I

SLOPE CONSTANTS OF POLYSTYRENE FRACTIONS

Benzoyl peroxide, %	Temperature, ° C.	$[\eta]$	k'
0.02*	60	2.11	0.38
0.02	60	2.00	0.34
0.10*	60	1.41	0.36
0.10	60	0.917	0.37
0.10	60	0.623	0.33
5.0 *	60	0.212	0.47
5.0	60	0.204	0.43
0.02*	120	1.080	0.40
0.02	120	1.025	0.38
0.02	120	0.747	0.35
0.00*	180	0.543	0.41
0.00	180	0.468	0.37
0.02*	180	0.405	0.42
0.02	180	0.391	0.46
0.02	180	0.265	0.42
.. †	Commercial	1.010	0.37
.. ‡	Emulsion	1.505	0.36
0.10§	60	1.249	0.36
1.0 §	60	0.609	0.37
5.0 §	60	0.233	0.39

**Head fraction.*
†Monsanto "Lustron" fraction.
‡Fraction from D. S. Montgomery.
§Unfractionated.

Preparation and Examination of Styrene–Divinylbenzene Copolymers

The amount of divinyl benzene required to cause the first appearance of gel was determined in exploratory experiments by adding graduated amounts to styrene at various levels of catalyst concentration. The polymerization mixtures were placed in stoppered test tubes and polymerized at 60° C. in a constant temperature bath. The resulting polymers were dissolved in toluene containing a small amount of inhibitor (phenyl-β-naphthylamine), twice precipitated and washed with methanol, and dried in a vacuum oven at 30° C. The low temperature drying and addition of inhibitor were necessary to prevent subsequent cross-linking of the polymer which still contained unreacted vinyl groups.

Viscosities of the unfractionated polymer were determined in the manner previously described. The presence of gel was immediately apparent on attempting to filter the solution through a fine sintered glass crucible. Typical results at low, medium, and high catalyst concentration are reported in Tables II to IV.

TABLE II

DETERMINATION OF GEL POINT, UNFRACTIONATED POLYMER, LOW CATALYST CONCENTRATION

Temperature, 60° C. Polymerization time, 15 hr.
Benzoyl peroxide, 0.10% Conversion, 20%

D.V.B., %	$[\eta]$	k'
0	1.249	0.36
0.019	1.352	0.37
0.031	1.365	0.36
0.050	1.531	0.42
0.062	Gel	....
0.091	Gel	....

TABLE III

DETERMINATION OF GEL POINT, UNFRACTIONATED POLYMER, MEDIUM CATALYST CONCENTRATION

Temperature, 60° C. Polymerization time, 15.5 hr.
Benzoyl peroxide, 1.00% Conversion, 39%

D.V.B., %	$[\eta]$	k'
0.00	0.609	0.37
0.091	0.855	0.41
0.119	1.011	0.42
0.171	Gel	....

TABLE IV

DETERMINATION OF GEL POINT, UNFRACTIONATED POLYMER, HIGH CATALYST CONCENTRATION

Temperature, 60° C. Polymerization time, 5.5 hr.
Benzoyl peroxide, 5.00% Conversion, 50%

D.V.B., %	$[\eta]$	k'
0.00	0.233	0.39
0.39	0.346	0.45
0.43	0.385	0.50
0.46*	0.400	0.44
0.52*	0.405	0.40

**Contained gel. Filtered twice through glass wool and sintered glass.*

The addition of D.V.B. did not alter the conversion, an indication that the polymerization rate was unaffected. The increase in intrinsic viscosity, however, is noteworthy, as is the greater amount of D.V.B. which can be added at higher catalyst concentrations before the onset of gel formation.

Using recipes like those described above, large batches of polymer were made with slightly less D.V.B. than that required to produce gel. All reactions were stopped immediately prior to the gel point as nearly as could be estimated, without particular consideration for the extent of conversion. It was necessary to use a large number of 25-ml. test tubes rather than one large container, since the reaction appeared to accelerate near the gel point and with inadequate heat dissipation a heavy gel resulted. Norrish and Brookman (19) observed a similar phenomenon when a polymerization medium became viscous.

The polymers were combined, purified, stabilized, and fractionated as before. Viscosities were measured as described previously for polystyrene, and the slopes and intrinsic viscosities determined from a plot of η_{sp}/C against C. Fig. 2 shows some typical experimental results for fractions prepared with

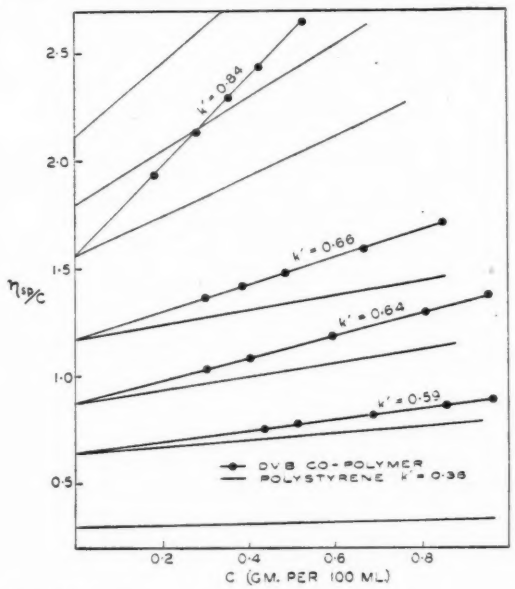

FIG. 2. *Effect of divinylbenzene on slopes of reduced viscosity–concentration lines.*

D.V.B., together with a line calculated for a normal polystyrene of the same intrinsic viscosity, to illustrate the marked difference in the viscosity–concentration relation. The calculation was made from the Huggins–Kraemer equation using a k' value of 0.38, the average of the results in Table I. In Fig. 3, $\log_{10}$ (slope) is plotted against $\log_{10}[\eta]$ for the branched polymers. The

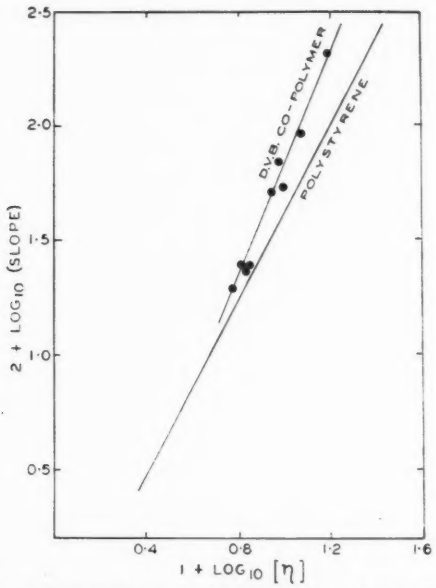

FIG. 3. *Comparison of slope and intrinsic viscosity relations of divinylbenzene copolymer with polystyrene.*

straight line which can be drawn through the points in this figure may be represented by a modified Huggins–Kraemer equation,

$$\eta_{sp}/C = [\eta] + 0.65\,[\eta]^{2.38}.$$

The linearity may be fortuitous, however, since it seems unlikely that all the reactions were stopped at precisely the same point close to, but before, gelation, and the tendency for reaction to accelerate in this region probably resulted in considerable heterogeneity of the polymers in respect of both extent of branching and molecular weight.

The k' values calculated by assuming conformity with the unmodified Huggins–Kraemer equation are listed in Table V.

TABLE V

SLOPE FACTORS OF CROSS-LINKED POLYSTYRENE (HEAD FRACTIONS)

Benzoyl peroxide, %	D.V.B., %	$[\eta]$	k' (Unmodified Huggins–Kraemer equation)
5.0	0.40	1.560	0.84
5.0*	0.40	1.175	0.66
3.0	0.20	0.991	0.54
3.5	0.25	0.942	0.77
4.0	0.30	0.888	0.64
4.5	0.30	0.701	0.49
4.5	0.35	0.666	0.51
5.0	0.45	0.650	0.59
4.0	0.30	0.589	0.55

**Second fraction.*

It is not possible to calculate accurately the molecular configuration without further information, but, assuming equal reactivity of all double bonds, a combining ratio of unity, and 50% conversion, the molecules contained in the order of 10 to 40 branch points per 10,000 styrene units.

Discussion

The present study has shown that over a range of intrinsic viscosities the k' value for polystyrene remains essentially constant, while copolymers of styrene and divinylbenzene have consistently higher k' values which increase with increasing intrinsic viscosity. In view of the known behavior of D.V.B. as a cross-linking agent, and the fact that the copolymers used were obtained immediately prior to onset of gelation, there can be little doubt that the higher k' values are due to cross-links, or branches in the copolymer molecule.*

This implies that the polystyrenes prepared in this study were essentially unbranched over the range of intrinsic viscosities studied, and that, in agreement with Simha's view, the increase in k' for copolymers of higher intrinsic viscosity corresponds to an increased amount of branching. The accompanying increase in intrinsic viscosity would then be attributed to a marked increase in molecular weight as a result of branching, the increase being so large as to more than offset the decrease in intrinsic viscosity which, according to Debye and Bueche, should result from branching.

The failure to detect a change in k' for head fractions of polystyrene polymerized at different temperatures is itself some indication that the normal polymer is not appreciably branched. The formation of a branch in polystyrene requires extraction of a hydrogen atom from the chain by a free radical, a reaction of higher activation energy than normal chain propagation. If branching occurred to any appreciable extent, the polymers prepared at higher temperatures should presumably have been relatively richer in branched species, and characterized by higher k' values. It should be noted, however, that the possible error in determining k' is greater at the lower intrinsic viscosities of polystyrenes prepared at higher temperatures.

Although there seems little doubt that the increase in k' observed in the present study with the styrene–D.V.B. copolymers is due essentially to branching, other factors might lead to a similar result. For example, fractions of polystyrene prepared in emulsion showed constant k' values in toluene, while in methyl ethyl ketone k' increased from 0.42 to 0.63 as the molecular weight increased (12), possibly as a result of progressively more coiling of the molecules. These data are plotted in Fig. 1 to yield a reasonable linear relation which can be represented by a modified Huggins–Kraemer equation.

$$\eta_{sp}/C = [\eta] + 0.56\,[\eta]^{2.30}.$$

The behavior of GR–S polymers of different conversions below the gel point can also be represented by a suitably modified equation (13).

*Flory (9, 10, 11) makes a distinction between the kinetics of branching and cross-linking. The terms are used interchangeably in the present paper because it is doubtful whether these lightly cross-linked polymers are experimentally distinguishable from branched polymers.

Since conformity with such a modified Huggins–Kraemer equation does not necessarily establish the influence of branching as distinct from, say, coiling, it would not seem possible to correlate the coefficient or exponent of $[\eta]$ with a specific change in configuration of the polymer molecule. It is perhaps preferable to retain the original equation, in which changes of shape are reflected only in k', and seek to determine the relative extents to which k' may be altered by factors other than branching.

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ELECTROKINETIC PROPERTIES OF CELLULOSE FIBERS

I. STREAM POTENTIAL AND ELECTRO-OSMOSIS[1]

By D. A. I. Goring[2] and S. G. Mason

Abstract

Stream potential, electro-osmotic, and permeability measurements were made on cotton pads in the presence of distilled water. Several sources of irreproducibility have been eliminated from the usual experimental methods of measuring the ζ-potential. Uniform packing of the pad has been shown to be important. The Briggs method of evaluating the "pore factor" by electrical conductivity measurements was found to be invalid. An alternative method of determining the factor is proposed, based on an assumed value for the pore orientation factor and an indirectly measured value of the swollen specific volume of the fibers. The latter can in principle be determined by measuring one of the electrokinetic functions or the permeability coefficient over a range of pad concentrations. When pads of different concentration were used, the stream potential, electro-osmotic, and permeability functions were found to vary erratically in the same manner, an effect which, it has been concluded, originates from lack of uniform packing of the pad. The electro-osmotic measurements were found to require a large correction for capillary electro-osmosis, a source of error which has been overlooked by other workers. The ratio of the ζ-potential calculated from electro-osmosis to that from the stream potential was greater than unity and increased with increase in pad concentration.

Introduction

Stream potential (2, 4, 6, 9), stream current (8), and electro-osmotic (3) methods have been used by a number of workers to calculate the so-called ζ-potential of cellulose fibers in the presence of aqueous electrolytes. With the exception of the recent measurements of Neale and Peters (8), anomalous results were reported and the general reproducibility was poor. Bikerman (1) has pointed out that much of the confusion in the published literature on this subject can be attributed to faulty techniques and misinterpretation of the experimental data.

The present work forms part of a project being undertaken in this laboratory to investigate the origin and significance of the surface charge of cellulose fibers. An accurate and convenient experimental method of measuring the charge was sought, and as a starting point it was decided to examine critically the existing methods of measuring the ζ-potential. A cell of conventional design was used to measure the stream potential, electro-osmotic flow rate, and permeability coefficient on the same pad of cellulose. A number of defects in the existing procedures for obtaining the necessary experimental data and in calculating the ζ-potential were revealed. These have led to a greatly improved experimental method which is described in the following paper of the series (5).

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Contribution from Pulp and Paper Research Institute of Canada and Chemistry Dept., McGill University, Montreal, Que.
[2] *Holder of a Studentship and a Fellowship under the National Research Council of Canada.*

In order that the implications of the experimental methods may be clearly understood, the essential ideas involved in calculating the ζ-potential of beds of unconsolidated particles by the stream and electro-osmotic methods are discussed below.

Basic Electrokinetic Equations

The stream current i generated when a liquid undergoes viscous flow through a single capillary of uniform cross section in an electrically charged solid, by the application of a pressure p, is given by the relation

$$i = \frac{pD\zeta a}{4\pi\eta L'} , \tag{1}$$

where ζ is the electrokinetic potential,
a and L' are the cross-sectional area and length of the capillary,
and D and η are the dielectric constant and viscosity of the flowing liquid.

If, instead of a hydrostatic pressure, an electrical potential difference E is applied across the ends of the channel, electro-osmotic flow will be established. When this occurs under conditions such that the pressure drop along the capillary is effectively zero, the volume rate of flow f becomes

$$f = \frac{ED\zeta a}{4\pi\eta L'} . \tag{2}$$

The derivation of these equations is well known and will not be given here. It is useful, however, to recall the assumptions upon which they are based. These may be outlined as follows:

(1) The space charge distribution in the liquid phase is determined by the Poisson equation

$$\nabla^2\psi = \frac{-4\pi\rho}{D} ,$$

ψ being the electrical potential and ρ the electric charge density at any point.

(2) The electrical potential at the solid surface is constant over the whole surface.

(3) The capillary diameter is so large compared with the dimensions occupied by the space charge in the liquid that a one-dimensional form of the Poisson equation is applicable.

(4) In streaming, a Poiseuille-type flow occurs and the entire space charge at any point in the liquid moves with the same velocity as the liquid at that point.

(5) In electro-osmosis the potential gradient of the externally applied field is constant throughout the capillary, and the electrical force acting on the space charge becomes operative as a shear force which overcomes the viscous drag of the liquid at the boundaries. In conjunction with assumption (3)

this leads to a pattern of "plug" flow, i.e., the fluid velocity is constant at all points across the capillary except near the walls where the entire velocity gradient is concentrated. This flow pattern is entirely different from that in streaming.

As was first clearly pointed out by Stern (12), ζ is the electrical potential, relative to the bulk liquid, at the surface of zero liquid velocity (and maximum rate of shear) and is not necessarily the potential of the bulk solid. Agreement in the ζ values by stream and electro-osmotic methods can therefore only be expected if the hydrodynamic surfaces are identical under the action of pressure and potential gradients. Rutgers and De Smet (11) have reported excellent agreement between the two methods in single glass capillaries of various sizes.

Equations (1) and (2) are generally derived for circular capillaries. Neale (7), however, has shown that Equation (1) applies to channels of arbitrary shape with the implied, but unstated, assumption that the velocity gradient normal to the envelope of zero liquid velocity is constant throughout the channel. It is readily shown that Neale's method can be extended to yield Equation (2).

Electrokinetic Equations for Porous Media

In a cylindrical bed of unconsolidated particles such as cellulose fibers, the pore structure consists of a complex network of interconnecting and tortuous pores of various sizes and shapes. Consider a layer of thickness dL in a pad of thickness L. The total streaming current I can be written by simple addition as

$$I = \frac{D\zeta}{4\pi\eta} \sum a \frac{dp}{dL'} ,$$

where the summation extends over all pores in the layer. If θ is the angle between the direction of a capillary and the axis of the pad,

$$\frac{dp}{dL'} = \frac{dp}{dL} \cos\theta .$$

If the pad is uniformly packed dp/dL can be replaced by p/L. Hence we have

$$I = \frac{pD\zeta}{4\pi\eta L} \xi , \tag{3}$$

where $\xi = \sum a \cos\theta .$

The geometrical factor ξ is subsequently referred to as the "pore factor."

When I is measured it is implied that no potential difference builds up across the pad. The leak-back current is therefore zero. On the other hand, when no charge is withdrawn from the system, a stream potential V is established through the pad structure such that the leak-back current through the pad balances the stream current. Thus from Equation (3),

$$V = \frac{pDR\zeta}{4\pi\eta L}\,\xi\ , \tag{4}$$

where R is the electrical resistance of the pad.

Similarly the rate of electro-osmotic flow F becomes

$$F = \frac{ED\zeta}{4\pi\eta L}\,\xi\ . \tag{5}$$

The Pore Factor

In applying Equation (3), (4), and (5) to calculate ζ from the experimentally observed quantities, it is necessary to evaluate the pore factor ξ.

In the classical Helmholtz–Smoluchowski method, it is assumed that the electrical conductance of the pad is due entirely to the liquid contained in the pores, and that the specific conductivity κ is the same as that of the bulk liquid. Under these conditions, the resistance R may be expressed as

$$\frac{1}{R} = \frac{\kappa}{L}\sum a\cos\theta = \frac{\kappa}{L}\,\xi\ . \tag{6}$$

Thus, for example, Equation (4) becomes

$$V = \frac{pD\zeta}{4\pi\eta\kappa}\ , \tag{7}$$

which indicates that V is independent of both the dimensions and condition of packing of the pad. This widely quoted equation is known to be invalid, particularly at low ionic concentrations, because of surface conductance effects which lead to pad resistances considerably less than given by Equation (6).

To overcome this complication, Briggs (2) measured the resistance R of the pad at high ionic concentrations where the surface conductance effect is presumed to become negligible. This yields a "pad cell constant" $C = \kappa' R'$, where κ' is the specific conductivity of the concentrated electrolyte. Thus from Equation (6)

$$\xi = L/C\ , \tag{8}$$

whence the substitution for the pore factor in the appropriate equation can be made. This procedure has been used extensively to determine the ζ-potential of cellulose and other fibers by the stream potential method. Bikerman (1) has criticized this approach by pointing out that in swelling gels such as cellulose and silk where ionic migration through the gel structure is possible, the paths for ionic transfer and fluid flow are not identical, and that the C value will therefore tend to yield a pore factor which is too high. Our experimental data (presented below) show the method to be invalid for cellulose fibers.

A more direct approach which we propose is an extension of the method of Neale (7) and involves purely geometrical considerations. Let v be the volume of a capillary per unit thickness of pad. Thus

$$a = v\cos\theta \quad \text{and} \quad \xi = \Sigma\, v\cos^2\theta\ .$$

If we assume that the distribution functions of pore size and pore orientation are independent of one another, we can then write

$$\xi = A\,\epsilon\,\overline{\cos^2\theta}\,, \tag{9}$$

where A is the area of the pad,

ϵ is the fractional volume of capillaries in the pad (the void fraction),

$$\frac{1}{A}\Sigma v\,,$$

and $\overline{\cos^2\theta}$ is averaged over all pores.

A certain amount of arbitrariness arises in the choice of an appropriate value of the orientation factor $\overline{\cos^2\theta}$. For flow through beds of spheres and cylindrical particles, Sullivan and Hertel (13) calculate $\overline{\cos^2\theta}$ to be 2/3 and 1/2 respectively. On the other hand, if the pore arrangement is completely random in three dimensions it is readily shown that $\overline{\cos^2\theta} = 1/3$. Neale (7), quoting Sullivan and Hertel, assigns a value of 0.79. The reasons for this choice are not clear. The value which we adopt here is 1/2, since this value has been shown on the basis of permeability studies (13) to be appropriate to the system of randomly packed cylindrical particles.

The void fraction ϵ can be written $(1 - \alpha c)$, where α is the swollen specific volume (cubic centimeters per gram) of the fibers and c is the concentration of solids in the porous bed (grams per cubic centimeter). The pore factor thus becomes

$$\xi = 1/2\,A(1 - \alpha c)\,. \tag{10}$$

Using this notation, the electrokinetic equations may therefore be written

Stream current function:

$$\frac{I\eta L}{pD} = \frac{A\zeta}{8\pi}(1 - \alpha c)\,. \tag{11}$$

Stream potential function:

$$\frac{V\eta L}{pDR} = \frac{A\zeta}{8\pi}(1 - \alpha c)\,. \tag{12}$$

Electro-osmotic function:

$$\frac{F\eta L}{ED} = \frac{A\zeta}{8\pi}(1 - \alpha c)\,. \tag{13}$$

In using these equations to calculate ζ, all quantities are known or can be determined experimentally except the swollen volume α. This is difficult to measure directly, especially in the case of natural fibers. If these equations are applicable, and the stream current/potential or electro-osmotic function is measured over a range of pad concentrations, ζ and α can be calculated from the intercepts of the straight line resulting when the appropriate electrokinetic function is plotted against the pad concentration c. Neale and Peters (8) used a modified form of Equation (11) but arbitrarily assumed $\alpha = 1$ for cotton fibers.

Useful information regarding the pore structure can be obtained from permeability measurements. The permeability coefficient K of a porous bed is given by the Kozeny–Carman Equation (13)

$$K = \frac{1}{kS_0^2} \frac{\epsilon^3}{(1-\epsilon)^2}, \tag{14}$$

where k is a combined shape-orientation factor,

S_0 is the surface presented to the flowing liquid per unit volume of bed material,

and ϵ is the void fraction term appearing in the stream and electro-osmotic equations given above.

Substituting for ϵ as above, Equation (14) becomes

$$(Kc^2)^{1/3} = \frac{1}{(k\sigma^2)^{1/3}} (1 - \alpha c), \tag{15}$$

where σ is the surface area per unit mass of bed material.

Measurements of K at different values of c can be used to determine α, in addition to σ, and the α thus computed should be identical with that in Equations (11), (12), and (13). Values of α found by Robertson and Mason (10) by the permeability method for water-swollen cellulose fibers varied from two to nine times the "true" specific volume (0.62 cc. per gm.), depending upon the previous history of the sample.

In the present study the methods of evaluating ξ from conductivity measurements using Equation (8) and the more direct methods of Equations (12), (13), and (15) have been examined.

General Experimental Methods

Materials

The pad material was obtained from a 1 lb. roll of Parke–Davis absorbent cotton. To facilitate pad formation, the cotton was cut into approximately 2-mm. lengths with a Wiley mill. The ash content before and after treatment in the mill was found to be 0.030% and 0.044% respectively, indicating that only slight impurities were introduced in the cutting process.

Distilled water was used as permeant in all stream and electro-osmotic experiments. The specific conductivity of the water after de-aeration varied from 1.0×10^{-6} to 1.2×10^{-6} ohm^{-1} cm.$^{-1}$.

The Stream Potential–Electro-osmotic Cell

The apparatus, as shown in Fig. 1, was similar to the stream potential cell described by Briggs (2).

The body of the cell was constructed of three square pieces of sheet Plexiglass which were bolted firmly together. The cellulose bed was located in a hole machined through the middle of the center block; the diameter and length of the hole were 3.006 cm. and 2.567 cm. respectively. The pad was

held between two 18-ct. gold electrodes (D) perforated with 12/cm.^{2} of diameter 0.08 cm. Two side pieces (E) supported the electrodes and also held sheet rubber washers against which the glass tubes (F) were clamped.

Pad Formation

The cellulose was soaked for 24 hr. in distilled water, and immediately before making a pad the suspension was dispersed for 15 min. in a British Standard Disintegrator.

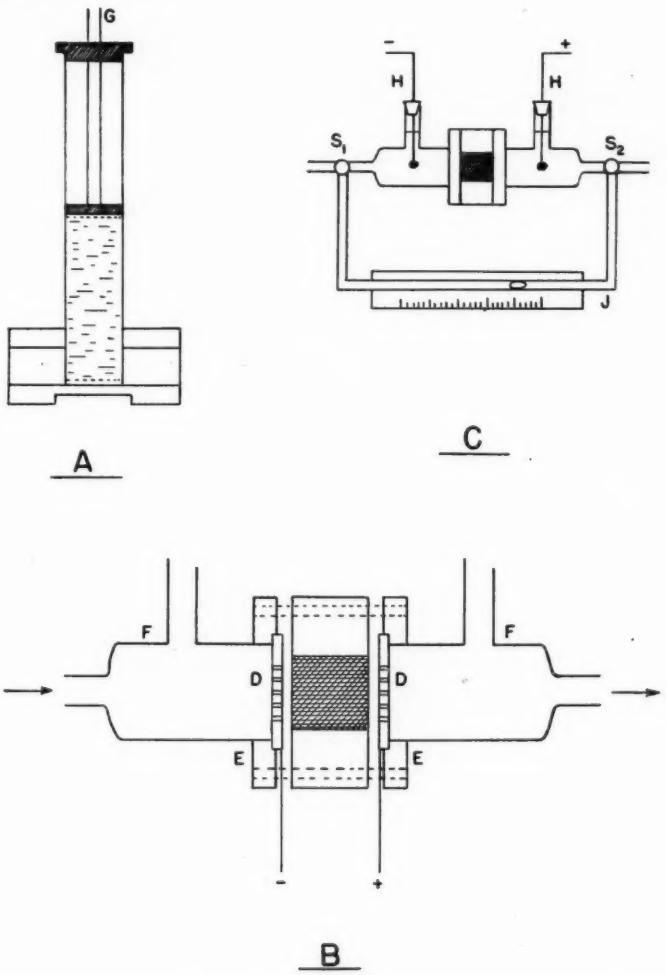

FIG 1. *The apparatus arranged for forming pad (A), stream potential (B), and electro-osmotic (C) measurements.*

A plunger-type apparatus constructed as an extension to the cell (see Fig. 1, *A*) was used to form the pad. A dispersed suspension of approximately 0.15% cellulose was poured through the glass tube, thus allowing the fibers to settle on a disk of 80-mesh copper gauze. The pad was then gradually compressed by means of a perforated brass plunger (*G*) fronted with 80-mesh gauze. After the pad had been washed, the copper gauze was removed and the cell reassembled as shown in Fig. 1, *B*.

Traces of air on the electrodes were found to cause large and variable residual potentials. Air bubbles were removed by filling the apparatus with warm air-free distilled water (50° C.) and boiling under reduced pressure. Proper deaeration was found to be essential in obtaining reproducible results, and its importance cannot be too highly emphasized.

Stream Potential and Permeability Measurements

Stream potential and permeability measurements were carried out simultaneously with the cell arranged as shown in Fig. 1, *B*. A supply of liquid under pressure was obtained by a gravity feed. The pressure across the pad was measured on a water manometer with a range of 95 cm. It was noted that pressures greater than this tended to compress and deform the pad. The rate of flow into a graduated cylinder was also measured.

A vacuum tube voltmeter (drawing about 10^{-10} amp.) in conjunction with a d'Arsonval galvanometer was used to measure the stream potential. The deflection obtained varied linearly with the applied potential, and a scale reading of 24 cm. was produced by an e.m.f. of 100 mv. The instrument was calibrated with a potentiometer. Usually a small variable potential of several millivolts was detectable when the pressure across the pad was zero. The residual potential was measured repeatedly during experiments and subtracted from the observed stream potential.

A 1000-cycle conductance bridge was used to measure the electrical resistance of the pad, which was of the order of 10^5 ohms.

The temperature of the effluent liquid was measured and appropriate values of η and D were used.

Electro-osmosis

When stream potential and permeability measurements had been completed, the apparatus was set up as illustrated in Fig. 1, *C*, and electro-osmotic experiments were carried out. A constant e.m.f. of 130 v. was applied to two auxiliary blacked-platinum electrodes *H* which were held in the side tubes by grooved corks. Free escape of the gaseous products of electrolysis was ensured by the grooves in the corks. The electro-osmotic current was computed from the potential drop across a known resistance in the circuit.

The electro-osmotic flow was followed by the movement of an air bubble along a calibrated capillary tube *J*.

Pad Cell Constant

On completion of stream potential, permeability, and electro-osmotic measurements, the pad cell constant C was determined by measuring the resistance of the pad when the liquid in it had been replaced by 0.005 N potassium chloride solution. The specific conductivity κ' of this solution was measured in a calibrated conductance cell.

The pad was then washed, dried at 105° C. for 24 hr. and weighed to the nearest milligram.

Development of Experimental Technique

Stream Potential and Permeability

In the early stream potential experiments it was noted that with prolonged flow through the pad the V/p ratio decreased. When the pressure was altered, a linear variation of V was obtained as shown in Fig. 2. On flow reversal, a further cycle of pressure change again yielded a straight line but the V/p ratio decreased. During these experiments a decay in the permeability coefficient was also noted.

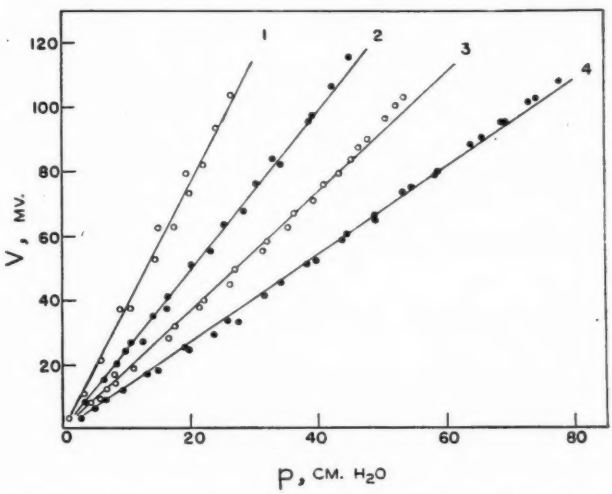

FIG. 2. *Linear relation between stream potential and pressure, in cycles in which the direction of flow was alternated. V/P decreases from cycle to cycle.*

Experiments were then initiated in which the pressure was kept constant and variations of K and $V\eta L/pDR$ with prolonged flow were studied. The flow was reversed at various intervals and the total volume of flow through the pad was recorded. As shown in Fig. 3, a considerable decay of K and $V\eta L/pDR$ occurred with increase of total volume of flow.

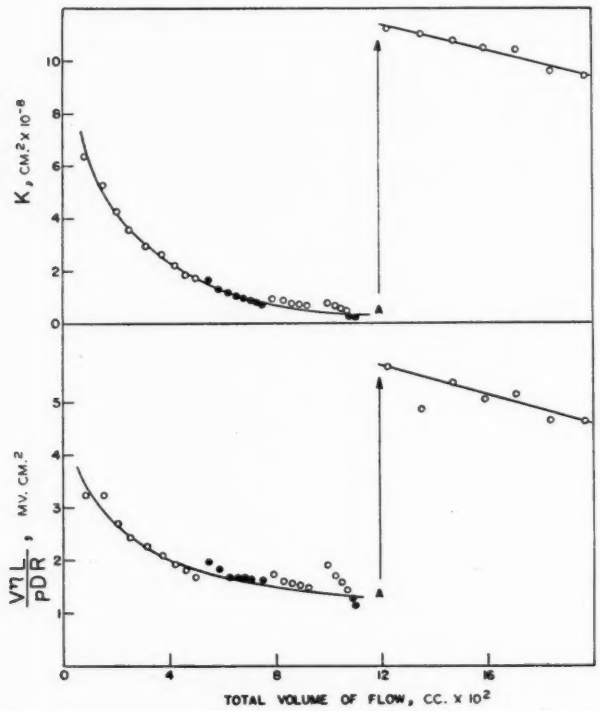

FIG. 3. *Decay of stream potential function and permeability with prolonged flow through the pad. At point A a thin section was removed from each face of the pad. Open circles denote flow in one direction and black circles in the other.*

When the permeability had fallen to a small fraction of the original value, the apparatus was dismantled and a thin section of cotton removed from each face of the pad. Each section represented about 1% of the weight of the pad. The cell was then reassembled and further measurements showed a large increase of K and $V\eta L/pDR$, but the subsequent decrease with prolonged flow was more gradual than previously observed. Apparently a "matting" effect was taking place, in which an impermeable layer was blocking the flow at either end of the pad.

Attempts were then made to discover the source of the matting effect. From the results of these experiments it was possible to eliminate the following as sources of the decay:

(1) Compression of the pad in the cell.

(2) Impurities in the permeant.

(3) The movement of very fine cellulose particles in the pad, and

(4) Back electro-osmotic effects.

The decrease was also independent of the time between measurements and was affected only by the total volume of flow through the pad.

It was concluded that the decay was due to a compression of the ends of the pad against the electrode which was magnified by the small fraction of electrode area available for liquid flow. To overcome this difficulty each end of the pad was faced with two layers of "Velon" plastic mesh with the weaves at an angle of 45°. This procedure was found to stop the matting completely. It is most important that this effect be eliminated. From Figs. 2 and 3 it is seen that gross changes in the stream potential function and permeability occur; such changes, if not properly interpreted, may produce wide variation in the calculated values of ζ and K. The decay effect has been observed by other workers (9) but there is no mention of corrective measures.

The thickness of the four layers of mesh was appreciable. In order to correct the electrical measurements, the space occupied by the mesh was assumed to contain only liquid. The true pad resistance was then the difference between the observed resistance and the computed resistance of the mesh space. The potential drop across the mesh layer was assumed to be zero and no correction was applied to the observed stream potential. It is probable that a small potential drop did exist, but, owing to the complexity of the stream current paths at the faces of the pads where current reversal occurs, the analysis was too complex to attempt to make a correction for this effect. Consequently the recorded potentials are probably too high. The pad cell constant was corrected by subtracting from the observed value a "mesh space cell constant" computed from the dimensions of the mesh space.

Electro-osmosis

Initially electro-osmotic measurements were carried out with the gold electrodes in the cell. The applied potential across the pad was computed from the electro-osmotic current and the resistance of the pad. Results obtained in this manner were irregular and R varied considerably during a single experiment. On prolonged electro-osmosis, gas bubbles appeared on the gold electrodes. This apparently resulted from the action of the electrodes as electrical "barriers" with one face of each electrode acting as a cathode and the other as an anode. When the gold electrodes were removed and replaced by perforated Lucite side pieces, reproducible results were obtained.

With the above technique the pad resistance could not be measured during electro-osmotic experiments; the following method was therefore adopted. When stream potential measurements were completed, simultaneous determinations were made of the pad resistance and the conductivity of the distilled water. During each electro-osmotic experiment the conductivity of the water used was observed.

The resistance of the pad during electro-osmosis was then obtained from

$$R_{osmosis} = R_{stream\ potential} \frac{K_{stream\ potential}}{K_{osmosis}}.$$

Experiments were then carried out to test whether stray electro-osmotic effects occurred when the cell did not contain a pad. An appreciable capillary electro-osmosis was found to occur. A careful investigation of this effect showed that the capillary electro-osmotic flow, F_c, was dependent on the length of the air bubble, increased with increase of capillary diameter, and was independent of the length of the capillary.

To correct for this effect, F_c was determined under standard conditions as an apparatus constant. A calibrated capillary of constant diameter (0.252 cm.) was used and five measurements of F_c were made using bubble lengths of 3.5 mm. to 5.5 mm. During every experiment the direction of electro-osmosis was reversed. A constant potential difference of 130 v. was applied across the platinum electrodes. The capillary electro-osmosis determined under these conditions was constant and the mean value of F_c was 12.3 ($\pm$ 0.3) $\times$ 10^{-4} cc. sec.$^{-1}$ towards the cathode, thus indicating a negative charge on the capillary walls. In all subsequent experiments with a pad in the cell the above conditions were duplicated exactly and the true rate of the electro-osmosis was obtained from

$$F_{true} = F_{observed} + 12.3 \times 10^{-4} \text{ cc. sec.}^{-1}.$$

The relative magnitude of F_c was high. In one pad the electro-osmosis was 30.4×10^{-4} cc. sec.$^{-1}$ and thus the correction represented 40% of the observed effect. This correction appears to have been overlooked by other workers.

A further correction was applied to allow for the back flow through the pad originating from the hydrostatic head required to maintain flow through the capillary. The magnitude of this effect was determined for each pad by measuring the permeability of the pad alone, as well as that of the pad and capillary system together. A correction factor was then applied to the observed flow; the values of this factor were between 1.03 and 1.10.

Pad Cell Constant

In the initial experiments the pad cell constant was determined with 0.1 *N* potassium chloride after the method of Briggs and subsequent workers (2, 4, 9). Anomalous results were obtained. Accordingly, experiments were carried out to determine the optimum concentration of electrolyte necessary to eliminate surface conductance effects in surgical cotton cellulose. Progressively stronger solutions of potassium chloride in distilled water were used as the liquid in the pad, the normality of each solution being determined conductometrically. A similar series of measurements was carried out without a pad.

The variation of the pad cell constant, *C*, with concentration of potassium chloride is shown in Fig. 4. For distilled water and dilute solutions of potassium chloride the specific conductivity of the pad was comparable to that of the bulk liquid, thus indicating a large surface conductance. With increas-

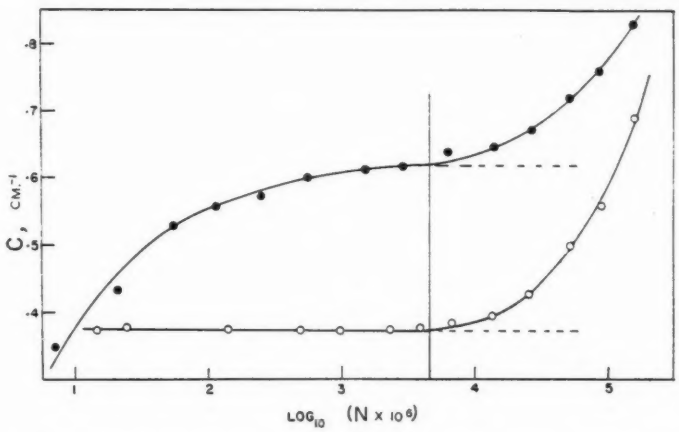

FIG. 4. *Variation of pad cell constant C with normality of potassium chloride solutions with (upper curve) and without (lower curve) a pad.*

ing concentration of electrolyte, surface conductance effects became less important and a greater part of the conductivity was due to the bulk liquid. The pad cell constant therefore increased until the normality reached such a value that surface conductance was no longer significant; C then remained constant. From Fig. 4 it is evident that, for the cell with a pad, C was effectively constant for solution strengths of 0.003 N to 0.005 N. Thus it was decided to use 0.005 N potassium chloride solution in obtaining the pad cell constant.

For concentrations greater than 0.005 N, a further increase in C was noted. The results of the control experiment without a pad showed a similar trend. It was therefore concluded that the further increase of C was not related to the presence of the cellulose but was probably due to a polarization effect on the surface of the gold electrodes. Clearly such effects may lead to serious errors when the pad cell constant is determined with 0.1 N potassium chloride.

Results

Stream potential, permeability, and electro-osmotic measurements were carried out on a series of pads of different concentration. Identical procedures following the methods previously described were used on each pad and in all experiments several observations were made in alternate directions of flow. The reproducibility on any one pad was good and the mean deviation of V/p, K, and F/E was usually $\pm$ 2%.

The ζ-potentials were computed from the pad cell constant C and the stream potential and electro-osmotic measurements, using the following equations, derived from Equations (4), (5), and (8).

$$\zeta_S = \frac{4\pi\eta VC}{pDR}, \tag{16}$$

$$\zeta_E = \frac{4\pi\eta FC}{ED}. \tag{17}$$

TABLE I

ZETA-POTENTIALS OBTAINED BY STREAM POTENTIAL AND ELECTRO-OSMOTIC METHODS USING THE BRIGGS (2) "PAD CELL CONSTANT"

Pad	c, (gm./cc.)	C, (cm^{-1})	ζ_S (mv.)	ζ_E (mv.)
1	0.162	0.568	−19.1	−23.3
2	0.174	0.558	−17.0	−19.4
3	0.183	0.583	−15.3	−19.7
4	0.195	0.608	−17.9	−24.3
5	0.197	0.604	−11.7	−15.9
6	0.207	0.636	−15.4	−22.3
7	0.215	0.635	−12.1	−18.8

The results are given in Table I. The following points will be noted:

(1) Both ζ_S and ζ_E vary erratically from pad to pad, although there is a general decrease in both values as the pad concentration increases.

(2) Values of ζ_E are significantly greater than ζ_S.

(3) The ratio ζ_E/ζ_S with one exception increases regularly with increased pad concentration. This is shown in Fig. 5.

(4) The cell constant C shows comparatively little variation with the packing density.

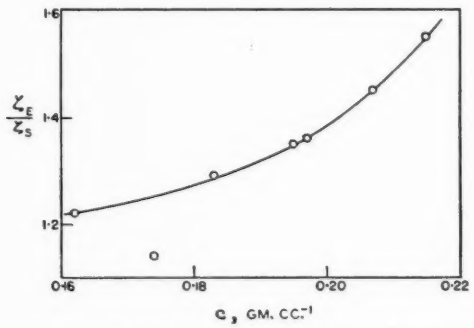

FIG. 5. *Variation of ζ_E/ζ_S with pad concentration.*

It is clear therefore that the Briggs method (2) using the pad cell constant C is not a valid method of evaluating the pore factor ξ, thus supporting the view of Bikerman (1).

According to Equations (12), (13), and (15) plots of the quantities $V\eta L/pDR$, $F\eta L/ED$ and $(Kc^2)^{1/3}$ against the pad concentration should yield straight lines. While the results, shown in Fig. 6, show a general linear trend, large deviations

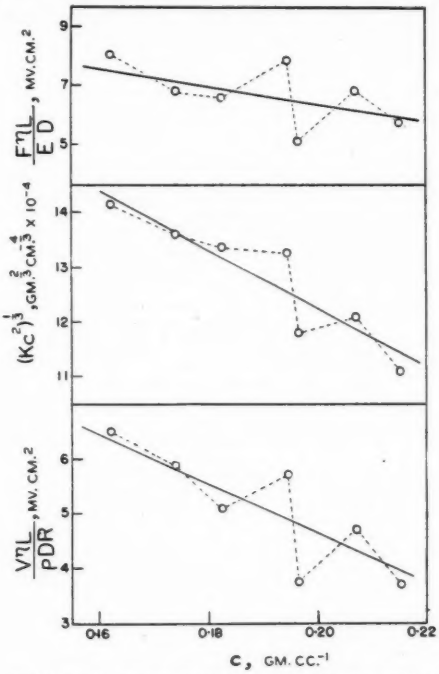

FIG. 6. *Irregular variation of stream potential, permeability, and electro-osmotic functions with concentration of the pad.*

persist from one pad to the next and reliable values of ζ and α cannot be calculated from the data. This irregularity contrasts sharply with the good agreement of the measurements for any one pad. It is interesting to observe the parallelism in the deviations for the three types of measurement. It is evident that an uncontrolled factor was affecting V/P, F/E, and K in the same manner. The most probable cause of these discrepancies is heterogeneity of the pad. Robertson and Mason (10) have noted a similar difficulty in their permeability measurements with cellulose pads. This was overcome by using a permeability cell with a piston arrangement such that the pad concentration could be varied continuously and a series of measurements carried out on a single sample. A stream current/potential cell embodying this principle is described in the following paper (5).

Discussion

The results show that if adequate precautions are taken, precise measurements of the stream potential and electro-osmotic flow rate can be made on any one pad. Electro-osmotic measurements are more tedious to carry out,

and require a number of corrections (chiefly capillary electro-endosmosis) which render the method less accurate than the stream method. The technique of using a cell of fixed pad dimensions, however, is unsatisfactory for determining ζ because of the difficulty of determining the pore constant. The failure of the Briggs method to provide a reliable value of ξ makes it necessary to seek other means of carrying this out. The more direct method proposed in the Introduction requires that measurements be carried out over a range of pad concentrations. Even if the pad formation technique could be improved, the use of a pad of fixed dimensions would prove laborious.

According to the theory, ζ_E/ζ_S should be unity and independent of the internal dimensions of the pad. While this discrepancy can be accounted for in part by experimental errors, the size and regularity of the discrepancy lead us to believe that the difference is real. Since Rutgers and De Smet (11) have found the ratio to be very close to unity with glass capillaries, we conclude the difference in ζ_E and ζ_S to be due to a basic imperfection of the theory in the case of swollen cellulose. Discussion of this point is deferred to a subsequent communication.

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ELECTROKINETIC PROPERTIES OF CELLULOSE FIBERS

II. ZETA-POTENTIAL MEASUREMENTS BY THE STREAM-COMPRESSION METHOD[1]

By D. A. I. Goring[2] and S. G. Mason

Abstract

A new technique of measuring the ζ-potential of cellulose fibers, in which stream current potential measurements are carried out over a range of solid concentrations on a single pad, is described. In employing the stream potential method it is necessary to measure the d-c. resistance of the pad, since a pronounced dispersion effect yields a-c. resistance values which are in considerable error. Reversible electrodes must therefore be used and since stream current measurements can then be carried out, this simpler method is preferred. Degrees of swelling calculated from the stream data are consistently higher than those calculated from permeability measurements. This discrepancy indicates a serious limitation of the conventional electrokinetic theory when applied to swollen cellulose. A model of the fiber–liquid interface, consisting of partially dissolved electrically charged cellulose chains accounting for the observed discrepancy, is discussed. If this model is applicable, the physical significance of the ζ-potential becomes extremely complex.

Introduction

In the first paper of this series (7) the theory of measuring the ζ-potential of cellulose fibers by streaming and electro-osmosis was discussed, and experimental data were presented, using both methods on pads of fixed dimensions. The conventional Briggs method (3) of evaluating the relevant internal pore dimensions in the swollen mass of fibers was shown to be unreliable. An alternative method based on measurements over a range of packing densities was proposed, but this was not found to be practicable in a cell of fixed dimensions.

In this paper we describe a compression type cell which allows stream measurements to be carried out over a range of concentrations on a single pad, following the method employed by Robertson and Mason (14) in applying the Kozeny–Carman permeability equation (16) to determine the specific surface of swollen fibers. This technique was found to yield reproducible stream current and stream potential measurements.

A careful study was made of the change of the stream potential function (7) with compression of the pad. With this cell, platinum electrodes were used and the pad resistance was measured at 1 kc.p.s.

In order to make observations with concentrated solutions of electrolyte, the compression cell was then fitted with silver – silver chloride electrodes and stream current measurements were made. The ζ-potentials obtained from

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Contribution from the Pulp and Paper Research Institute of Canada and Chemistry Department, McGill University, Montreal, Que.
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stream current data were considerably lower than those previously obtained by the stream potential method. This discrepancy was found to originate from a frequency dependence of the pad resistance which yielded erroneously low resistance values when a-c. bridge methods were used.

Stream current observations were made and the ζ-potential and the swollen specific volume calculated by the intercept method previously discussed (7). Permeability measurements were also carried out and the effective specific volume and specific surface of the fibers were computed (14). In all experiments the specific volume obtained from the stream data was greater than that obtained from the permeability. The origin of this discrepancy is uncertain; but an explanation is suggested, using an alternative model of the fiber–liquid interface, based on the concept of partial solution of the cellulose molecules at the phase boundary.

The symbols used below are those which we have defined previously (7).

Experimental Part

Materials

Surgical cotton and "standard" cotton were used in the earlier stream potential experiments. The sample of surgical cotton was the same as that previously used (7). Three batches of "standard" cotton were prepared from samples of high-grade raw Texas, Brazilian, and Mexican cotton. The method of preparation was that of Worner and Mease (18).

A large supply of commercial bleached unbeaten sulphite pulp was used as pad material in the stream potential and later stream current experiments. Each sample of pulp was soaked for 60 hr., dispersed in a British Standard Disintegrator for 5 to 10 min., and finally washed with six liters of distilled water before use.

The Compression Cell

The cell is shown in Fig. 1, and in its final form it resembled that of Neale and Peters (11). The pad was held between two perforated electrodes which fitted snugly into a Fischer and Porter precision bore Pyrex glass tube 2.558 cm. in diameter.

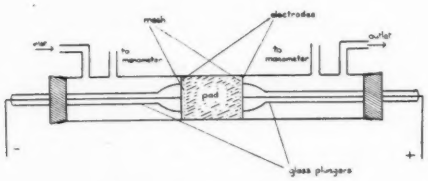

FIG. 1. *The compression cell.*

The platinum electrodes were perforated with 9.4 holes per sq. cm. of diameter 0.6 mm., and the silver with 5.5 holes per sq. cm. of diameter 1 mm. In both cases the two electrodes were machined from the same stock to minimize residual potential effects.

The electrodes were mounted on glass plungers with platinum leads entering the cell through the holes in the capillaries. At the ends of the tube, rubber stoppers were used to support the plungers. The length of the pad was altered manually by sliding the plungers through the stoppers.

The silver electrodes were chloridized by electrolysis in 0.1 *N* hydrochloric acid solution using a platinum cathode and a current density of 4 ma. per sq. cm. The current direction was reversed several times at intervals of one hour. A final layer of chloride was then deposited by anodizing the silver for one hour. Formed in this manner, the electrodes were stable and gave residual currents which never exceeded 0.03 μamp.

Pad Formation

The cell without the electrodes was clamped in a vertical position and a perforated brass plunger was set about 16 cm. above the lower end. The pad was formed by pouring a 4 liter suspension containing about 3 gm. of cellulose through the apparatus. Before inserting the electrodes, layers of plastic mesh were placed at the ends of the pad to prevent matting (7). Dispersion of the suspension and deaeration of the pad were carried out as described before (7).

In the experiments with thorium chloride solutions, it was found necessary to re-pass the solution through the pad after formation in order to establish a true sorption equilibrium. This solution was then used as permeant. If such precautions were not taken, additional sorption of thorium ions occurred during the run and appreciable changes of stream current and potential with time were observed.

Stream Current, Stream Potential, and Permeability Measurements

The pad was compressed in stages and, at each pad concentration, stream potential and permeability observations were carried out, using the platinum electrodes. Measurements of permeability coefficient and the stream potential were made as previously described (7).

Stream current experiments were carried out in the same way except that the reversible electrodes were used. The current was measured on a calibrated d'Arsonval galvanometer with a sensitivity of 0.003 μamp.mm.$^{-1}$ and a resistance of 400 ohms. A correction was made for the slight leak-back of current through the pad due to the resistance of the galvanometer.

Resistance Measurements

A well shielded Jones conductance bridge with a CRO null detector for a-c. measurements and a galvanometer for d-c. measurements was used to measure

pad resistances. The range of the bridge (0–60,000 ohms) was extended with two General Radio decade resistances having ranges of 0–0.1 megohm and 0–1 megohm. These were placed in series with the variable arm.

D-c. resistance measurements were made at current densities of the same order of magnitude as the stream currents. To correct for residual electrode polarization currents, the d-c. measurements were made in both directions and the mean value used.

Results

Stream Potential and Permeability Experiments (Platinum Electrodes)

A number of stream potential–compression and permeability–compression experiments were carried out on pads of cotton and bleached sulphite pulp, using the platinum electrodes. In these experiments the resistance of the pad was measured at 1000 c.p.s. As mentioned in the Introduction, it later became apparent that the values so determined were in error and, as a result, the calculated values of ζ obtained in these measurements were subject to a certain degree of uncertainty. However, a brief discussion of the data is presented in order to illustrate certain interesting trends.

TABLE I

STREAM POTENTIAL AND PERMEABILITY RESULTS OBTAINED WITH PLATINUM ELECTRODES

(Pads 1, 2 and 3 refer to stream potential plots shown in Fig. 3)

Pad	Type of cellulose	Permeant	ζ, mv.	a from stream potential, cc./gm.	a from permeability, cc./gm.	σ, sq. cm./gm. $\times 10^{-3}$
..	Surgical cotton	KCl (10^{-4} N)	−32.5	1.60 ± 0.05	1.30 ± 0.05	5.4
..	" "	" "	−32.4	1.70 "	1.30 "	5.3
..	Standard " (Texas)	" "	−31.4	1.70 "	1.20 "	5.4
..	" " "	" "	−30.5	1.80 "	1.10 "	5.8
..	" " (Brazilian)	" "	−31.8	1.50 "	1.20 "	4.9
..	" " "	" "	−30.5	1.70 "	1.10 "	5.5
..	" " (Mexican)	" "	−25.8	1.40 "	1.00 "	4.8
..	" " "	" "	−25.2	1.30 "	1.20 "	4.5
..	Bleached sulphite pulp	" (2.5×10^{-5} N)	−29.4	3.30 "	2.50 "	14.1
1	" " "	" "	−28.8	3.30 "	2.50 "	14.5
2	" " "	$ThCl_4$ (2×10^{-5} N)	−17.2	3.30 "	2.30 "	14.0
3	" " "	" (4×10^{-5} N)	− 5.5	3.30 "	2.20 "	13.0

NOTE.—The ζ-values in this table are erroneously high. For explanation see text.

Table I summarizes the results obtained. Plots of $V\eta L/pDR$ against the pad concentration c yield straight lines. From these plots, values of ζ and the effective specific volume, a, of the swollen fibers were obtained by the intercept method (7). The regularity of these curves is in marked contrast to the erratic curves from the cell of fixed pad dimensions previously described (7).

Fig. 2 shows a typical plot for a cotton pad, and Fig. 3, several plots for bleached sulphite pulp pads. With the sulphite pulps, the linearity is broken when the pad concentration exceeded 0.15 gm. per cc.

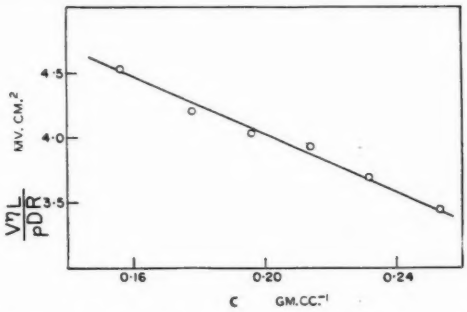

FIG. 2. *Variation of VηL/pDR with pad concentration for Texas standard cotton. The VηL/pDR and c intercepts correspond to* $1/a$ *and* $A\zeta/8\pi$ *respectively* (7).

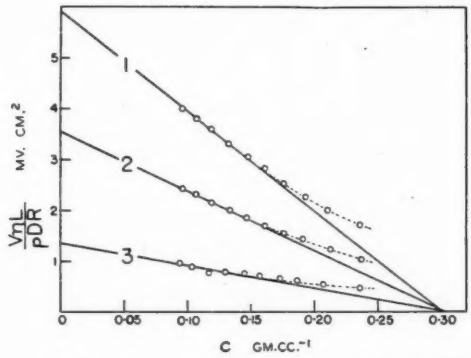

FIG. 3. *Effect of varying* ζ *upon stream potential, using pads of sulphite pulp. The calculated* ζ *and* a *values are given in Table I.*

A comparison of the ζ values for the duplicate pads (Table I) shows that the reproducibility is good. Values of a are somewhat more variable.

The permeability data show a similar consistency. For both cotton and sulphite pads the $(Kc^2)^{1/3}$ versus c curves are linear (Figs. 4 and 5), thereby confirming the Kozeny–Carman equation as modified by Robertson and Mason (7, 14). The swollen volumes and specific surfaces obtained from this equation, using Fowler and Hertel's value of 5.55 for the shape-orientation factor (6), are included in Table I.

Sulphite pulp pads were found to yield more uniform and reproducible variation of the stream potential and permeability functions on compression than the cotton pads. This was due mainly to the difficulty of making uniform

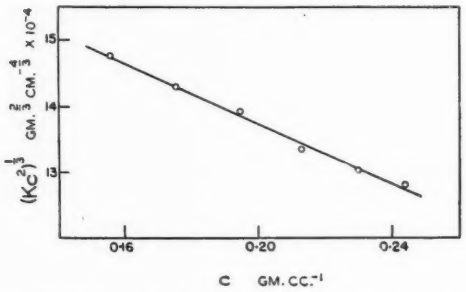

FIG. 4. *Variation of* $(Kc^2)^{1/3}$ *with pad concentration for Texas standard cotton. The c and* $(Kc^2)^{1/3}$ *intercepts correspond to* $1/a$ *and* $(1/5.55\sigma^2)^{1/3}$ *respectively* (7, 14).

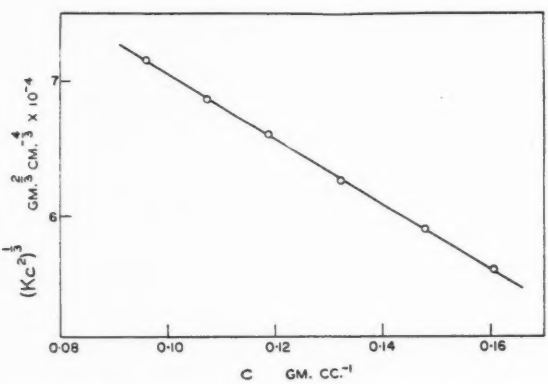

FIG. 5. *Variation of* $(Kc^2)^{1/3}$ *with pad concentration for bleached sulphite pulp.*

pads from cotton suspensions. Sulphite pulp with shorter and more flexible fibers was found to be a more suitable material for pad formation and compression.

An essential requirement of the theory (7) is that when ζ is varied, the stream potential function lines should converge on identical c intercepts corresponding to a constant a value. This is shown in Fig. 3 for the bleached sulphite pulp, using thorium chloride to decrease the ζ-potential.

It will be noted that the stream potential data in all cases yield a values which are significantly greater than those calculated from permeability data. According to the theory these values should be identical. This discrepancy is also shown in the more accurate results presented below, and is discussed later.

Stream Current and Stream Potential Experiments

The sensitivity of the stream potential method dropped considerably when relatively high ionic concentrations of electrolyte were used. It was considered to be an important part of the theory to demonstrate that the α value obtained by this method was independent of ζ, provided no significant change in the degree of swelling occurred. While this was demonstrated for small changes in ζ (Fig. 3), a test of the theory was desired for an actual reversal in the sign of the potential. When this was done with thorium chloride the resistance values became so low that accurate measurement of the stream potential was difficult. It was therefore decided to adopt the stream current technique, using the reversible silver – silver chloride electrodes, since the sensitivity of this method is independent of the resistance of the pad.

In the initial experiments, which were carried out on the bleached sulphite pulp, it was noted that the values of ζ calculated by the intercept method, while consistent within themselves, were lower than those obtained from the stream potential measurements given in Table I. To permit a direct comparison, stream current and stream potential measurements were carried out on the same pad of sulphite pulp with 2.5×10^{-5} N potassium chloride solution. The pad resistance was determined at 1 kc.p.s. (R_{1000}) and also with d-c. (R_0).

From the results given in Table II it is seen that R_{1000} is considerably lower than R_0. On the other hand there is fair agreement between R_0 and the ratio $V/p: I/p$. This agreement indicates that R_0 is essentially equal to the resistance offered to the back current when a stream potential is generated. Closer agreement than that shown in Table II has since been obtained in some more precise experiments (2).

TABLE II

STREAM CURRENT AND STREAM POTENTIAL RESULTS ON A PAD OF SULPHITE PULP WITH 2.5×10^{-5} N POTASSIUM CHLORIDE SOLUTION AS PERMEANT

c, gm./cc.	V/p, mv./cm. H_2O	I/p, amp./cm. $H_2O \times 10^9$	$V/p: I/p$, ohms $\times 10^{-3}$	R_0, ohms $\times 10^{-3}$	R_{1000}, ohms $\times 10^{-3}$
0.095	0.998	5.71	175	165	132
0.106	1.012	6.00	169	160	126
0.119	0.888	6.22	143	138	107
0.135	0.797	6.36	125	119	92
0.156	0.658	6.26	105	99	75

At 1 kc.p.s. the pad develops an added conductance which causes R_{1000} to be lower than the true direct current resistance of the pad. The effect of this discrepancy in the determination of the ζ-potential is shown in Fig. 6. The graph of $I\eta L/pD$ against pad concentration is linear and ζ, calculated by the intercept method, is -22.8 mv. The $V\eta L/pDR_{1000}$ vs. c curve is also linear,

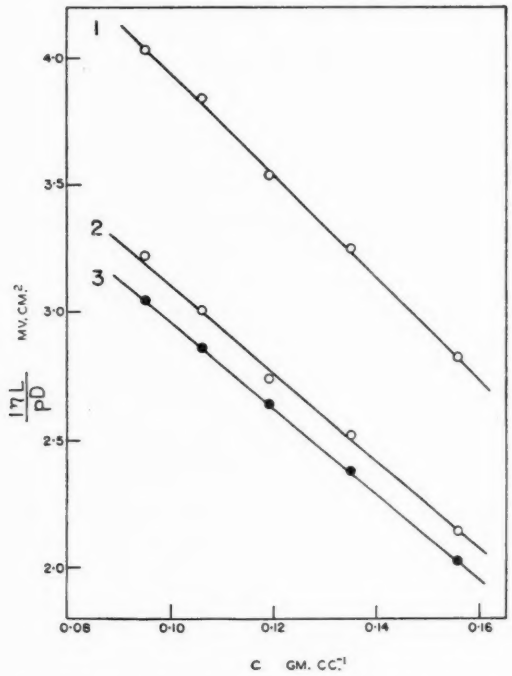

FIG. 6. *Stream potential (Curve 1 using R_{1000}, Curve 2 using R_0) and stream current (Curve 3) for pads of sulphite pulp.*

but because of the low values of R_{1000} the ordinates have increased and ζ equals -28.8 mv. which is identical with the value obtained under similar conditions, using the platinum electrodes (pad 1, Table I). When $V\eta L/pDR_0$ is plotted against the pad concentration, the straight line obtained is almost coincident with the stream current plot and ζ is found to be -23.5 mv. The slightly higher values of $V\eta L/pDR_0$ may well arise from an error in V owing to the unknown potential drop across the mesh space (7).

It is therefore clear that the d-c. resistance value of the pad must be used in the stream potential equation.

Stream Current and Permeability Experiments

A series of stream current and permeability measurements were carried out on the bleached sulphite pulp, for which the negative ζ-potential was decreased progressively by means of potassium chloride solutions of increasing concentration and reversed by use of thorium chloride. The results are summarized in Table III. Good reproducibility in the ζ-potentials is shown in the duplicate measurements with 10^{-4} N and 10^{-3} N potassium chloride solutions.

TABLE III

STREAM CURRENT AND PERMEABILITY RESULTS FOR SULPHITE PULP USING VARIOUS SOLUTIONS OF ELECTROLYTES AS PERMEANTS

Pad	Permeant	ζ, mv.	a from stream current, cc./gm.	a from permeability, cc./gm.	σ cm.²/gm. × 10^{-3}
0	KCl 2.5×10^{-5} N (Table II)	−22.8	3.65	2.45	16.1
1	KCl (10^{-4} N)	−25.9	3.75	2.45	16.7
1a	" "	−26.2	3.70	2.55	15.9
2	" (10^{-3} N)	−20.2	3.90	2.45	15.6
2a	" "	−19.5	4.00	2.45	16.0
3	" (5×10^{-3} N)	−13.2	3.90	2.50	14.7
4	" (2×10^{-2} N)	− 8.8	4.05	2.30	14.4
5	$ThCl_4$ (1.4×10^{-4} N)	+21.5	3.65	2.45	14.9
6	" (2.1×10^{-4} N)	+26.4	3.70	2.45	14.9

The stream current – pad concentration plots are shown in Fig. 7. Good linearity is shown at pad concentrations below 0.15 gm. per cc., but at higher concentrations the slope tends to decrease in the same manner as was found with the stream potential plots.

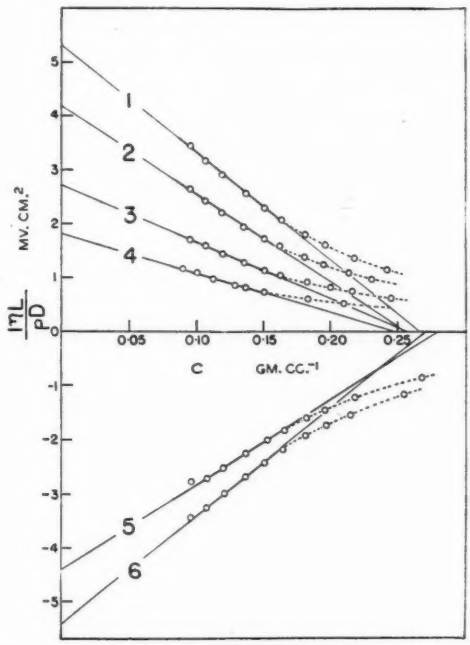

FIG. 7. *Stream current plots for pads of sulphite pulp, using different concentrations of electrolyte. The calculated ζ and a values are given in Table III.*

The σ values shown in Table III are slightly greater than those found for the same sample (Table I) in the stream potential experiments. This can be attributed to the greater time of disintegration in the preparation of these pads. This was increased from 5 to 10 min. and was found to improve the uniformity of the pad. The gradual decline in σ with decreasing (negative) potential is believed to be significant but cannot be accounted for at the present time. The straight line portions of stream current – pad concentration curves (Fig. 7) over the range of potentials from -25.9 to $+26.4$ mv. show reasonably good convergence upon a common c-axis intercept, confirming the observations of the stream potential measurements discussed above.

It should be noted that the dispersion effect leads to small α values when R_{1000} and the stream potential method are used. Thus the discrepancy between the more accurate α values computed from stream current measurements (Table III) and from permeability measurements is further enlarged.

It is evident that a maximum in the negative ζ-potential occurs between 10^{-4} N and 10^{-3} N potassium chloride. A similar maximum was noted but not reported in earlier measurements with cotton (7). Rabinov and Heymann (13) and Neale and Peters (11) have reported similar maxima. The last named authors attributed the effect to impurities in the electrolyte, and considered it to be spurious since it cannot be accounted for on the basis of the conventional Gouy–Chapman diffuse layer theory for the case where ion adsorption does not occur. We concur however with the view (13) that this maximum in ζ is real, and must be accounted for in any complete theory of the electrokinetic phenomena of cellulose.

Discussion

It is clear that the stream–compression method of evaluating the pore factor ξ (7) yields reproducible values of the ζ-potential, provided the pad is uniformly deposited and compressed, and occluded gases and pad end-effects are absent. It is important that the fibers be flexible so that a sufficiently wide range of void fractions can be obtained. For this reason it has not been possible to apply the method to nonswelling fibers such as glass wool and asbestos.

In applying the stream potential method, however, it is important to use the d-c. resistance value of the pad, because of the considerable dispersion effect which may reach 25% between 0 and 1000 c.p.s. and which appears to be general for water swollen cellulose (8).

Most of the ζ values for cellulose reported in the literature have been determined by the Briggs stream potential method (3), using pad resistances which have been obtained invariably by a-c. methods. Thus there are two errors inherent in the method, one resulting from the pad cell constant which leads to abnormally high values of the pore factor (7) and hence to low values of ζ, and the other to low resistance values and hence to high values of ζ. It is highly unlikely that the two errors will cancel each other. In order to de-

termine R_0, reversible electrodes are necessary, in which case stream current measurements can also be made. The stream current method holds two important advantages. (1) Greater accuracy is possible especially at high concentrations of electrolyte when stream potentials become inaccessibly small. (2) The experimental procedure is simpler, since no resistance measurements are necessary and a galvanometer replaces the vacuum tube voltmeter and conductance bridge. On the other hand the reversible electrodes restrict the measurements to electrolytes containing a common anion (in this case Cl^-).

The large and consistent discrepancy between the a values from stream and permeability methods indicates a basic weakness in the theory, and clearly must be explained. The remainder of our discussion deals with this point.

The results of Fowler and Hertel (6) on nonswollen fibrous materials show that the a determined from the gas permeability method is, within the limits of experimental accuracy, identical with the true specific volume of the material of the bed. The liquid permeability studies of Robertson and Mason (14) on swollen cellulose confirm this. Further, the "permeability" a values for the cottons in Table I show excellent agreement with swollen volumes computed from the results of Preston and Nimkar (12), using a centrifuging technique. Thus it is reasonably certain that the "permeability" a is the true swollen volume of the fibers in the pad. On the other hand the constancy of the a value from stream measurements over a range of ζ-potentials (Figs. 3 and 7) indicates that some fundamental significance must be attached to this quantity.

The assumptions involved in deriving the electrokinetic equations were discussed previously (7). An important assumption is that the dimensions of the space charge are negligible compared with the diameter of the capillaries through which flow occurs. If this is not valid it is conceivable that the observed difference in a might result.

The equivalent Helmholtz-layer thickness δ of the Gouy–Chapman diffuse layer (1) is given by

$$\delta = \sqrt{\frac{RTD}{8\pi e^2 N\mu}} , \tag{1}$$

where R is the gas constant,
N is Avogardo's number,
D is the dielectric constant of the liquid,
e is the electronic charge,
and μ is the conventional ionic strength, $\frac{1}{2}\sum n_i z_i^2$, of the bulk liquid.

The equivalent pore radius $\bar{r}$ can be computed from permeability data, using the following simplified form of the Kozeny–Carman equation (5)

$$\bar{r} = 2\sqrt{\frac{k.K}{\epsilon}} = \frac{2(1 - ac)}{\sigma c} . \tag{2}$$

For the series of sulphite fiber pads given in Table III, the value of $\bar{r}$ is 5.5×10^{-4} cm. at a pad concentration of 0.15 cc. per gm., the maximum concentration for linearity of the stream current function.

The corresponding values of δ and $\bar{r}/\delta$ are given in Table IV. For all pads the pore radius is much greater than δ. Verwey and Overbeck (17) in an exhaustive theoretical study of the interaction of adjacent diffuse layers showed that no distortion of the space charge distribution of a single isolated layer is caused by bringing a similar layer within a distance of 5δ.

TABLE IV

APPROXIMATE THICKNESS OF THE DIFFUSE IONIC LAYER FOR VARIOUS ELECTROLYTE CONCENTRATIONS

Permeant	δ, cm. $\times 10^8$	$\frac{\bar{r}_{0.15}}{\delta}$
KCl (10^{-4} N)	300	180
" (10^{-3} N)	100	550
" (5×10^{-3} N)	40	1370
" (2×10^{-2} N)	20	2700
$ThCl_4$ (1.4×10^{-4} N)	160	340
" (2.1×10^{-4} N)	130	420

It is therefore unlikely that the differences in α can be attributed to the layer thickness effect.

Similarly we conclude the effect of wall curvature to be negligible and the use of the one-dimensional form of the Poisson equation justified (7).

It is interesting to note that other workers (11, 13) have used the layer thickness effect to account for the decrease in the ζ-potential observed with increased pad concentration. Such differences can be more easily attributed to incorrect values of the pore factor ξ given by the Briggs method (7), and the erroneously low value for the degree of swelling assumed by Neale and Peters (11).

The discrepancy cannot be accounted for on the basis of a distribution of pore sizes. The magnitude of the stream effect through a simple circular capillary varies with r^2. The volume rate of Poiseuille flow, on the other hand, varies as r^4. It was thought possible that the substitution of $\overline{r^4}$ by a term such as $(\overline{r^2})^2$ might account for the difference. An analysis, which we do not reproduce here, showed however that identical values of α should still result.

In order to resolve the anomaly, it is necessary to return to the model of the solid–liquid interface used (7) in deriving the conventional electrokinetic equations. The electrical charge on the solid is assumed to be distributed in such a way that the electrical potential at the surface of the Stern layer (15) is everywhere constant, and that the space charge outside of this layer is completely free to move with the same macroscopic velocity as the fluid.

Clearly such a representation in the case of a swollen polymeric material such as cellulose is highly idealized. Cellulose is believed to consist of an assembly of flexible linear chain molecules whose length may be as great as several microns, held together by lateral hydrogen bonding and Van der Waals' forces in amorphous and crystalline regions (10). In the theory of swelling of cellulose by water originally proposed by Campbell (4), surface molecules of amorphous cellulose are considered to be anchored to the body of the structure, with a portion of the molecule or a group of molecules "dissolved" and free to move as a unit in the water in a restricted Brownian movement.

With this concept in mind, an alternative model of the ionic distribution at the fiber–liquid interface is tentatively advanced. Instead of a sharp boundary of the Stern type (15) we propose that there is a diffuse boundary of considerable thickness called the β-layer, in which partially dissolved molecules and groups of molecules, bearing an electrical charge, extend into the liquid; each such unit is surrounded by its own Gouy–Chapman diffuse double layer whose equivalent thickness δ is small compared with the length of the chain. A highly idealized representation is shown in Fig. 8. In streaming and electroosmosis, only the free space charge in each Gouy–Chapman layer is capable of movement, since the partially dissolved chains are restrained. It will be seen that this mechanism permits a semiquantitative explanation for the discrepancy in α.

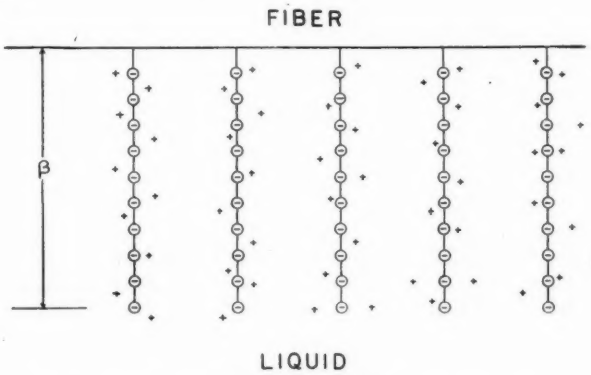

FIG 8. *Possible distribution of ions at the fiber-liquid interface.*

Consider now viscous flow through a cylindrical capillary of radius r and length L' under the action of a pressure p. For simplicity we assume (1) that the macroscopic distribution of positive and negative charges through the β-layer is uniform, (2) that the space charge is confined to this layer, and (3) that the fixed "solid" groups in the layer do not disturb the Poiseuille-type velocity profile. It may be argued that the latter assumption is inadmissible, since the partially dissolved chains will have the effect of resisting flow, but unless this simplification is made the analysis becomes difficult.

The velocity, u_x, of the annulus x from the wall is given by

$$u_x = \frac{p}{4\eta L'} (2r - x)x .$$

The stream current can then be written

$$i = \int_0^\beta 2\pi (r - x)\, u_x . q . dx ,$$

where q is the volume density of the mobile charges in the β-layer.

Substituting for u_x and integrating over the layer

$$i_s = \frac{\pi p q \beta^2}{2\eta L'} \left(r - \frac{\beta}{2}\right)^2 . \tag{3}$$

For a bed containing N identical parallel capillaries per unit area the total stream current I becomes

$$I = \frac{A\pi p q \beta^2}{2\eta L'} \sum_0^N \left(r - \frac{\beta}{2}\right)^2 , \tag{4}$$

where A is the total cross-sectional area of the bed.

Defining the fractional free area ϵ_β as

$$\epsilon_\beta = \sum_0^N \pi \left(r - \frac{\beta}{2}\right)^2 , \tag{5}$$

Equation (4) can be written

$$I = \frac{A p q \beta^2}{2\eta L'} \epsilon_\beta . \tag{6}$$

For a macroscopically uniform pad of cellulose fibers consisting of a randomly oriented network of pores of various sizes Equation (6) becomes (7)

$$I = \frac{A p q \beta^2}{2\eta L} \epsilon_\beta \overline{\cos^2\theta} , \tag{7}$$

where L is the pad thickness
and θ is the angle between the direction of a pore and the axis of the pad.

From the definition given in Equation (5) ϵ_β represents the void fraction available for liquid flow less the volume of a layer of liquid of thickness $\beta/2$ on the surface of the fibers.

Thus

$$\epsilon_\beta = (1 - a_\beta c) , \tag{8}$$

where a_β is the effective specific volume of the fibers plus a layer of liquid of thickness $\beta/2$ around each fiber. Thus a_β may be expected to exceed the true specific volume a_K (determined from permeability coefficient measurements) by the volume of this layer. If β is assumed small compared with the fiber diameter, we may write

$$\frac{\beta}{2} = \frac{a_\beta - a_K}{\sigma} , \tag{9}$$

where σ is the external surface area per unit mass of fiber.

By combining Equations (7) and (8) and substituting the value 1/2 for $\overline{\cos^2\theta}$ (7), the stream current function becomes

$$\frac{I\eta L}{p} = \frac{Aq\beta^2}{4}(1 - a_\beta c)\,. \tag{10}$$

Thus a straight line should result when $I\eta L/p$ is plotted against the pad concentration c and having intercepts $1/a_\beta$ and $Aq\beta^2/4$.

In Table V, β, $q\beta^2$, and q are given for the sulphite pads on which stream current measurements were carried out (Table III). The value of β is that calculated from the average experimental a_β and a_K using equation (9).

TABLE V

CALCULATED VALUES OF $q\beta^2$ AND q FOR THE SULPHITE PADS GIVEN IN TABLE III. MEAN $\beta = 1.78 \times 10^{-4}$ CM.

Permeant	$q\beta^2$, e.s.u./cm. $\times 10^4$	q, electron charges/cm.^{3} $\times 10^{-12}$
KCl (10^{-4} N)	−10.30	−67
" (10^{-3} N)	− 8.12	−53
" (5×10^{-3} N)	− 5.27	−35
" (2×10^{-3} N)	− 3.50	−23
$ThCl_4$ (1.4×10^{-4} N)	+ 8.60	+56
" (2.1×10^{-4} N)	+10.50	+69

The value of β (1.8×10^{-4} cm.) so calculated corresponds to a cellulose chain consisting of about 3500 anhydroglucose units. Molecular groups or fibrils, several microns in length, are clearly discernible in electron-microscope images of the surface of unswollen fibers (9). Thus the calculated β is not unreasonable, especially in view of the approximate nature of the analysis made above.

A comparison of $\frac{\overline{r_{0.09}}}{\beta}$ and $\frac{\overline{r_{0.15}}}{\beta}$ may serve to explain the marked curvature of the stream current plot for the higher pad concentrations. At the lower concentration the mean pore radius is 6 times as great as β. At 0.15 gm. per cc. the ratio is only about 3, so that the β-layer now occupies an appreciable portion of the pore space. On further compression q may be caused to increase and a_β to decrease. Such an effect would cause the observed curvature in the stream potential plot.

In this method of analysis the term $q\beta^2$ corresponds to $D\zeta/2\pi$ computed from the conventional stream current equation. Since β for one sample is appreciably constant, q is proportional to the conventional ζ value. On the basis of the mechanism proposed, however, the physical interpretation of the significance of q and ζ is not understood at the present time, but is believed to be complex.

From these results the model shown in Fig. 8 may be claimed successful in interpreting the difference in the specific volume as obtained by stream current and permeability methods.

The model can also be used to account for the pronounced dispersion of the electrical resistance at low frequencies (8). Curiously enough, the model fails to account for the observed increase in the ratio of the ζ determined from electro-osmosis to that determined from stream potential measurements previously reported. Discussion of this aspect of problem, however, is deferred to a later communication.

It must be emphasized that such a model does not represent the complete picture of the boundary layer and that the analysis of streaming is only approximate. It is possible that a combination of the diffuse layer and the "dissolved" chains exists, each contributing to the ionic distribution at the interface.

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ELECTROKINETIC PROPERTIES OF CELLULOSE FIBERS

III. NOTE ON THE LOW FREQUENCY DISPERSION OF ELECTRICAL RESISTANCE[1]

By D. A. I. Goring,[2] G. J. Biefer,[3] and S. G. Mason

Abstract

Sulphite cellulose, rayon cellulose, and silk fibers in the presence of 10^{-4} *N* potassium chloride show a 20 to 25% decrease in electrical resistance between 0 and 100 c.p.s. An additional but smaller decrease occurs between 100 and 15,000 c.p.s. The systems also show a marked capacitive reactance. Reversal of the sign of the ζ-potential in sulphite fibers destroys the effect. Non-swelling fibers such as asbestos, glass, and acetate rayon, slightly swelling nylon, and moderately swelling wool show no comparable behavior. It is evident that the phenomenon is related to the swelling properties of the systems, but it cannot be concluded whether it is associated with the surface or the interior of the swollen fibers.

Introduction

This note deals briefly with the low frequency dispersion effect which we first observed in the course of measuring the conventional ζ-potential of cellulose fibers by the stream current and stream potential methods (5). In a pad of bleached sulphite fibers it was found that an increase in the electrical conductivity of the pad of the order of 25% occurred between 0 and 1000 cycles.

Bikerman (1) predicted that the portion of surface conductance due to electro-osmotic transfer is frequency dependent and should decrease as the frequency increases. Rosenhead and Miller (8) in a rigorous theoretical analysis of the surface conductance in a conventional Gouy–Chapman diffuse layer showed that no appreciable dispersion should be observed below frequencies of 10^5 c.p.s., i.e., the dispersion region is of the same order as that of the Debye–Falkenhagen effect in strong electrolytes (3). Rabinov and Heymann (7) believed that they confirmed this conclusion when they found no difference in the resistance of cotton pads between 60 and 1000 c.p.s.

In view of this apparent discrepancy it was considered to be of interest to confirm and extend our original observations. This was done in a series of exploratory experiments described below, using a number of different fibrous materials.

Experimental

Impedance measurements were carried out in the stream compression cell fitted with reversible silver – silver chloride electrodes, using the Jones bridge (5). A Clough–Brengle low frequency oscillator and a C.R.O. detector (100 to 15,000 c.p.s.) were used in the a-c. measurements. D-c. measurements were carried out as previously described (5).

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Contribution from the Pulp and Paper Research Institute of Canada and Chemistry Department, McGill University, Montreal, Que.
[2] *Holder of a Studentship and a Fellowship under the National Research Council of Canada.*
[3] *Holder of a Bursary under the National Research Council of Canada.*

Results

The resistance R_f and the equivalent shunt capacitance C_f of a typical run on a pad of bleached sulphite pulp in $2.5 \times 10^{-5}N$ potassium chloride are shown in Table I. The sulphite pulp was identical with that used previously (5).

TABLE I

DISPERSION EFFECT IN A PAD OF SULPHITE PULP IN PRESENCE OF 2.5×10^{-5} N POTASSIUM CHLORIDE

Pad concentration 0.102 gm./cc. and pad length 5.29 cm.

Frequency c.p.s.	R_f, ohms $\times 10^{-2}$	R_0/R_f	C_f, $\mu\mu f$.
0	1020	1.00	
100	838	1.22	700
200	825	1.24	320
400	814	1.25	170
800	804	1.27	95
1000	802	1.28	81
2000	794	1.29	59
4000	788	1.30	49
8000	783	1.31	44
15,000	781	1.31	41

A marked increase in both R_f and C_f occurs with increase in frequency. It is evident, however, that the most pronounced change occurs in the region between 0 and 100 c.p.s. Unfortunately this range could not be investigated because of the limitations of the oscillator and detector. Furthermore, the capacitance values are nominal only, since in the Jones bridge the shunt capacitance is used merely as a balancing device and not for the purpose of accurate measurement. These values have been included however to illustrate an effect which was subsequently found to be perfectly general, i.e., systems showing a pronounced increase of R_f also show a marked increase in C_f with decreasing frequency.

For these reasons the data reported here are not amenable to accurate quantitative analysis, but permit only a qualitative interpretation. As a matter of convenience the factor R_0/R_f is subsequently taken to indicate the magnitude of the dispersion effect.

In Fig. 1 the variation of R_0/R_f with frequency is shown for a number of resistors (described in Table II) having R_0 values of the same order of magnitude. With the carbon resistor R_0/R_f was constant and equal to unity, thus indicating that the effect was not generated in the leads or the bridge circuit. The small increase of R_0/R_f for the cell containing electrolyte alone was probably due to a slight polarization of the electrodes during the d-c. measurements. Such polarization would lead to a high reading for R_0. When a sulphite pulp pad was in the cell a marked increase of R_0/R_f was noted. On compressing the pad to higher pad concentrations the effect became even more marked. It can

be concluded therefore that the low frequency dispersion effect previously described (5) is associated with the cellulose, and is not a spurious effect arising from faulty shielding or electrode polarization.

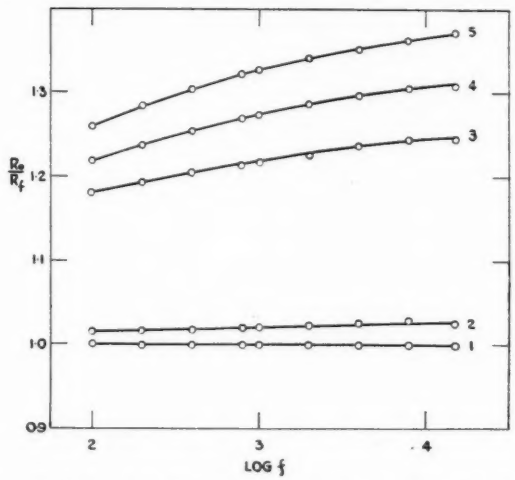

FIG. 1. *Variation of R_0/R_f with frequency of systems given in Table II.*

TABLE II

RESISTORS CORRESPONDING TO CURVES GIVEN IN FIG. 1

Curve	Resistor	R_0, ohms	Pad concentration, gm./cc.	Length of pad, cm.
1	Carbon	108,700	—	—
2	Cell + KCl (2.5×10^{-5} *N*)	137,300	—	3.71
3	Cell + sulphite pulp + KCl (2.5×10^{-5} *N*)	148,600	0.072	7.48
4	Cell + sulphite pulp + KCl (2.5×10^{-5} *N*)	102,050	0.102	5.29
5	Cell + sulphite pulp + KCl (2.5×10^{-5} *N*)	71,500	0.150	3.58

A few observations were made at different values of the ζ-potential of the sulphite pulp pad in the presence of potassium chloride and thorium chloride. The ζ-potentials were determined by the stream current method (5). The resistance measurements were made at a pad length of 3.0 cm. and a pad concentration of 0.18 gm. per cc. The results are given in Table III where the magnitude of the dispersion effect is shown as R_0/R_{1000}. When the fibers were negatively charged, the dispersion effect was high, but on reversing the charge with thorium ions the effect became negligible. The disappearance of the dispersion effect on reversal of the charge was checked by repeating the measurements on different pads prepared from the same sample of sulphite pulp.

TABLE III

VARIATION OF FREQUENCY EFFECT WITH CHANGE OF ζ-POTENTIAL OF SULPHITE PULP

Permeant	R_0, ohms $\times 10^{-3}$	R_0/R_{1000}	ζ, mv.
2.5×10^{-5} N KCl	72	1.33	−22.8
1×10^{-4} N KCl	41	1.31	−25.9
1.4×10^{-4} N $ThCl_4$	53	1.04	+21.5
2.1×10^{-4} N $ThCl_4$	35	1.03	+26.4
2.5×10^{-5} N KCl (without pad)	137	1.02	—

Table IV shows the results of a series of measurements on a miscellaneous assortment of fibrous materials in the presence of 10^{-4} N potassium chloride. For comparison, measurements on 10^{-4} N potassium chloride alone have been included. The magnitude of the dispersion effect is represented by R_0/R_{100}, R_0/R_{1000}, and $R_0/R_{15,000}$. Asbestos, glass wool, nylon, acetate rayon, wool, and cotton show no significant effect. On the other hand, surgical cotton exhibits a marginal effect, while silk and viscose rayon show a comparatively large change which is of the same order as that of sulphite fibers under the same conditions. As with sulphite fibers, the most marked decrease in resistance occurs in the region between zero and 100 c.p.s.

TABLE IV

DISPERSION EFFECT OF MISCELLANEOUS FIBROUS MATERIALS IN 10^{-4} N POTASSIUM CHLORIDE

Pad material	Mass of pad, gm.	Length of pad, cm.	R_0, ohms $\times 10^{-2}$	R_0/R_{100}	R_0/R_{1000}	R_0/R_{15000}
(10^{-4} N KCl)	—	5.04	521	1.02	1.02	1.04
Asbestos	4.50	3.85	304	1.03	1.04	1.07
Glass wool	2.93	3.3	399	1.06	1.07	1.08
Nylon	4.10	3.75	712	1.02	1.03	1.07
Acetate rayon (acetyl value 54)	4.32	4.30	674	1.02	1.03	1.06
Wool	3.17	3.98	440	1.04	1.04	1.06
Surgical cotton	3.35	3.55	457	1.05	1.06	1.15
Silk	4.40	3.85	354	1.20	1.22	1.24
Viscose rayon	3.33	3.85	310	1.19	1.23	1.27

Discussion

These results, while fragmentary, illustrate several interesting points. (1) When dispersion of the electrical resistance occurs, the effect is most marked at low frequencies, indeed in a region which is not normally covered in dispersion measurements. At the same time, an appreciable capacitive

reactance is exhibited, the equivalent shunt capacitance increasing as the frequency is decreased. The systems are therefore roughly equivalent to a series resistance–capacitance network in parallel with a resistance, the latter corresponding to the measured d-c. resistance. (2) Swelling is a necessary but not sufficient condition for the low frequency phenomenon we have described. Asbestos, glass, and acetate rayon (non-swelling) show no significant dispersion. Sulphite pulp, silk, and viscose rayon which undergo appreciable swelling in water show a pronounced dispersion, while wool and positively charged sulphite fibers do not. With cotton the effect if any is small; this accounts for the failure of Rabinov and Heymann (7) to detect dispersion in their measurements.

The phenomenon cannot be accounted for by the conventional theory of surface conductance in a Gouy–Chapman diffuse layer (8). Any dispersion arising from this mechanism would lead to an increase in resistance with increasing frequency.

Fricke and Curtis (4) have reported an analogous dispersion effect in aqueous suspensions of butterfat, latex, mineral oils, and kaolin over the frequency range 0.25 to 2000 kc.p.s. and conclude that it arises from a polarization phenomenon at the particle–liquid interface. We cannot conclude whether a similar mechanism is operative here, or whether it arises from the restricted motion of adsorbed ions in the interior of the swollen gels after the manner postulated by Murphy and Lowry (6) or whether it is a form of the Maxwell–Wagner dielectric relaxation effect (9).

One possibility upon which it is interesting to speculate is based on the concept of "partially dissolved" molecular chains at the surface and in the interior of swollen fibers (5). These chains are assumed to bear an electrical charge and to be capable of limited movement in an electrical field. In an a-c. field the charges may oscillate continuously and behave like a series resistance–capacitance network, the electrical resistance component being related to the hydrodynamic resistance to motion of the molecules and the capacitance to the restoring force generated when the molecule is displaced from its normal equilibrium position. Upon removal of the electrical charge on the molecules the effect will disappear. This model accounts partially for the effect of thorium ions upon R_0/R_{1000} of sulphite fibers, although it is difficult to explain why the dispersion effect disappears upon reversal of the charge without making additional assumptions regarding the manner in which the thorium ions are distributed in the fiber.

The existence of the dispersion effect invalidates much of the published data on the ζ-potential of swelling fibers determined by the Briggs stream potential method (2), as we pointed out previously (5).

A complete interpretation of the phenomenon is undoubtedly complex, but we believe it to be a potentially useful approach to the study of swelling phenomena in fibrous materials.

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